Estimation of Exposure to Persons in California to Phosphine due to Use of Aluminum Phosphide, Magnesium Phosphide, and Cylinderized Phosphine Gas

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by

Ian Reeve, Staff Toxicologist (Specialist)

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California Environmental Protection Agency
Department of Pesticide Regulation
Worker Health and Safety Branch
1001 I Street, P.O. Box 4015
Sacramento, California 95812-4015
www.cdpr.ca.gov

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Table of Contents

ABSTRACT

Aluminum phosphide, magnesium phosphide, and phosphine are the active ingredients in 25 products currently registered for use in commodity, space, spot, and burrowing pest fumigations. Phosphine can be applied directly or via aluminum phosphide or magnesium phosphide, which are solids that degrade upon contact with moisture in the air to generate phosphine gas. The exposure estimates generated in this document are organized according to the type of fumigation or aeration, followed by the type of structure, if applicable, and the exposure scenario (e.g., applicator, aerator, occupational bystander, or residential bystander). The peak phosphine exposure estimates presented below consist of short-term and seasonal exposure estimates. In cases where exposure data were available, the short-term estimate for the worker was derived from the highest measured air concentration. This air concentration was corrected for recovery if the field fortification study yielded a sample recovery of less than 90%. The air concentration was then multiplied by the product label maximum application rate and then divided by the application rate used in the exposure study. The seasonal exposure estimate for the worker consists of the mean of the measured air concentrations. These air concentrations were corrected for recovery, if the field fortification study yielded a recovery of less than 90%, multiplied by the estimated seasonal application rate, and divided by the application rate used in the exposure study. In cases where data was lacking, the exposure estimate was derived from the permissible exposure limit listed on the product labels, or from surrogate exposure estimates. If applicable, the estimates were adjusted for the use of proper respiratory protection. For each estimate, percutaneous absorption of phosphine could not be quantitated. As a result, the exposure estimates listed in this exposure assessment document may underestimate exposure, especially for scenarios where the worker is located in an enclosed area.

The exposure estimates associated with commodity fumigation were generated for 8 different types of structures: concrete upright bins in grain-elevators, farm bins, flat storage facilities, warehouses, bulk cars, box cars, ship holds, and ship containers. For the grain-elevator, the highest exposure estimates for the applicator, occupational bystander, and residential bystander are 0.12 ppm (12-hr TWA), 0.2 ppm (9.7-hr TWA), and 0.1 ppm (24-hr TWA), respectively. The corresponding estimates for the farm bin are 0.1 ppm (8-hr TWA), 0.3 ppm (8-hr TWA), and 0.1 ppm (24-hr TWA). In addition, the peak exposure estimate for the aerator is 0.3 ppm (8-hr TWA). The corresponding estimates for the flat storage facility are 0.1 ppm (8-hr TWA), 0.3 ppm (8-hr TWA), 0.1 ppm (24-hr TWA), and 0.3 ppm (8-hr TWA). For the warehouse, the corresponding exposure estimates are 0.04 ppm (8-hr TWA), 0.3 ppm (8-hr TWA), 0.1 ppm (24-hr TWA), and 0.3 ppm (8-hr TWA). In addition, in the exposure study for this structure, spent fumigant was retrieved following the fumigation. The highest exposure estimate for this worker that retrieves spent fumigant is 0.12 ppm (8-hr TWA). The peak exposure estimates for the applicator, aerator, occupational bystander, and residential bystander associated with commodity fumigation and aeration in the bulk car are 0.04 ppm (8-hr TWA), 0.08 ppm (8-hr TWA), 0.1 ppm (8-hr TWA), and 0.1 ppm (24-hr TWA), respectively. The corresponding exposure estimates for commodity fumigation and aeration in the box car are 0.08 ppm (8-hr TWA), 0.1 ppm (8-hr TWA), 0.3 ppm (8-hr TWA), and 0.1 ppm (24-

hr TWA). For commodity fumigation in ship holds, the peak exposure estimates are 0.1 ppm (8-hr TWA), 0.08 ppm (8-hr TWA), and 0.2 ppm (8-hr TWA) for the applicator, aerator, and occupational bystander, respectively. The corresponding exposure estimates for commodity fumigation and aeration within the ship container are 0.08 ppm (8-hr TWA), 0.06 ppm (8-hr TWA), and 0.3 ppm (8-hr TWA).

In addition to commodity fumigation, exposure estimates were generated for scenarios associated with spot fumigation. The peak estimates for the applicator, occupational bystander, and residential bystander are 0.004 ppm (8-hr TWA), 0.3 ppm (8-hr TWA), and 0.1 ppm (24-hr TWA), respectively. In addition, in the exposure study for spot fumigation, a worker aerated the fumigated equipment, and retrieved and deactivated the spent fumigant. The peak exposure estimate for this worker is 0.02 ppm (8-hr TWA).

Along with commodity and spot fumigation, exposure estimates were generated for scenarios associated with burrowing pest fumigation. The exposure scenarios included for this type of application are the applicator, reentry worker, and occupational bystander. The peak exposure estimates generated for these scenarios are 0.24 ppm (8-hr TWA), 0.06 ppm (8-hr TWA), and 0.03 ppm (8-hr TWA), respectively.

The California Air Resources Board (CARB), pursuant to the provisions of AB 1807 and AB 2728, identifies phosphine as being a toxic air contaminant. Per DPR policy, in addition to estimating bystander exposure for individuals located within or near the facility or field being treated, bystander exposure to ambient phosphine due to fumigant application was also assessed. Exposures to phosphine in ambient air are anticipated to be equal to or less than bystander exposures, as the highest pesticide concentrations in air occur adjacent to an application.

INTRODUCTION

The Department of Pesticide Regulation (DPR) is charged with protecting individuals and the environment from potential adverse effects that may result from the use of pesticides in the state of California. This is codified in the California Food and Agriculture Code (CFAC), Sections 11501, 12824, 12825, 12826, 13121-13135, 14102, and 14103. As part of DPR's effort to meet this mandate, pesticide active ingredients (AI's) are prioritized for assessment of exposure and risk potential. Prioritization of AI's is conducted by the Adverse Effects Advisory Panel, a group of senior scientists from the Worker Health and Safety, Medical Toxicology, and Environmental Monitoring Branches of DPR and from Cal/EPA's Office of Environmental Health Hazard Assessment. A description of the risk prioritization process can be found at DPR's website (http://www.cdpr.ca.gov/docs/risk/raprocess.pdf). When comprehensive risk assessments are initiated for particular AI's, the evaluations are conducted in accordance with California Code of Regulations Title 3, Section 6158 (3 CCR 6158). The subjects of this exposure assessment document (EAD), aluminum phosphide, magnesium phosphide, and phosphine, are fumigants applied to control rodents, and insect pests in raw agricultural and non-food commodities, animal feed, and processed foods.

Numerous phosphine and phosphine-generating products have been applied in California. Currently, 25 products contain or generate phosphine gas with 18 of the products containing aluminum phosphide, 5 of the products containing magnesium phosphide, and 2 of the products consisting of pressurized gas mixtures containing phosphine (Tables 1 - 3).

Table 1. Aluminum Phosphide Products

Product Form	Brand Name	% Aluminum Phosphide	Registration Number
granules for use in QuickPHlo-R® phosphine generator	QuickPHlo-R® Granules	77.5	70506-69-AA
gas-permeable blister packs of tablets	Phostoxin® Tablet Prepac	55	72959-9-AA
	Phostoxin® Prepac Rope	55	72959-8-AA
gas-permeable bags of fumigant	Detia® Fumex	57	72959-10-AA
	Weevil-Cide® Gas Bags	60	70506-15-AA
	Gastoxin® Fumigation Sachet	57	43743-3-AA
	Gastoxin® Fumigation Sachet Chain	57	43743-3-ZA
pellets	Fumitoxin®	55	72959-2-ZA
	Phostoxin®	55	72959-5-AA
	Weevil-Cide®	60	70506-14-AA
	DetiaPhos®	55	72959-5-ZA
	Gastoxin®	57	43743-2-AA
tablets	Weevil-Cide®	60	70506-13-AA
	Fumitoxin®	55	72959-1-ZA
	PhosFume®	60	70506-13-AA-1015
	Phostoxin®	55	72959-4-ZB
	DetiaPhos	55	72959-4-ZA
	Gastoxin®	57	43743-1-AA

Table 2. Magnesium Phosphide Products

Product Form	Brand Name	% Magnesium Phosphide	Registration Number
granules for use in Degesch phosphine generator	Magtoxin® Granules	94.6	72959-11-AA
gas-permeable blister pack of pellets	Magtoxin® Prepac Spot Fumigant	66	72959-7-AA
gas bags	Magnaphos®	66	70506-17-AA
plates impregnated with magnesium phosphide	Magtoxin® Fumi-Cel	56	72959-6-AA
	Magtoxin® Fumi-Strip	56	72959-6-ZA

Table 3. Cylinderized Phosphine Gas Products

Brand Name	% Phosphine	Registration Number
ECO_2FUME® Fumigant Gas	2	68387-7-AA
$VAPORPH_3$OS® Phosphine Fumigant	99.3	68387-8-AA

Phosphine is most likely to induce toxicity following inhalation. Phosphine has a vapor pressure of 2.93×10^4 mmHg at 25º C (HSDB, 2011), and can react with moisture in the lungs to generate phosphoric acid, causing edema (NIOSH, 1999). Laboratory studies have shown that phosphine inhibits mitochondrial respiration, damages hemoglobin, and induces oxidative stress (HSDB, 2011). Air concentration limits have been established at both the state and federal levels for phosphine (Table 4).

Table 4. Phosphine Air Concentration Limits

Organization	Phosphine Air Concentration Limit	ppm	mg/m^3
OEHHA	chronic inhalation reference exposure level	0.0006	0.0008
Cal/OSHA	PEL (exposure duration = 8 hours TWA)	0.3	0.4
	STEL (exposure duration = 15 min. TWA)	1	1
OSHA	PEL (exposure duration = 8 hours TWA, for a 40-hr workweek)	0.3	0.4
NIOSH	REL (exposure duration of up to 10 hours TWA, for a 40-hr workweek)	0.3	0.4
	ST (exposure duration = 15 min TWA)	1	1
	IDLH	50	
EPA (IRIS)	inhalation RfC		0.0003

Cal/OSHA: California Occupational Safety and Health Administration, California Department of Industrial Relations
EPA (IRIS): Environmental Protection Agency (Integrated Risk Information System)
IDLH: immediately dangerous to life or health
Inhalation Reference Concentration (RfC): an estimate with uncertainty spanning perhaps an order of magnitude of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime
NIOSH: National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, Dept. of Health and Human Services
OEHHA: Office of Environmental Hazard and Health Assessment, California Environmental Protection Agency
OSHA: Occupational Safety and Health Administration, U.S. Dept. of Labor
PEL: permissable exposure level (the maximum permitted 8-hour time-weighted average concentration of an airborne contaminant) during a 40-hr work week
REL: recommended exposure limit
ST: short-term exposure limit
STEL: short-term exposure level - [a 15-minute time-weighted average exposure which is not to be exceeded at any time during a workday even if the 8-hour time-weighted average is below the PEL]

A Reregistration Eligibility Decision (RED) document was generated in December 1998 by the United States Environmental Protection Agency (U.S. EPA) for aluminum phosphide and magnesium phosphide. Aluminum phosphide and magnesium phosphide were first registered as pesticides in the U.S. in 1958 and 1979, respectively. Since these pesticides were registered before 1984, amendments to the Federal Insecticide, Fungicide, and Rodenticide Act require that they undergo a risk assessment using more recent scientific and regulatory standards.

For certain exposure scenarios, different approaches were taken in estimating exposure to phosphine in the RED and EAD. The RED utilized a task force study completed by the registrants to estimate exposure for various scenarios associated with commodity fumigation in different structures including the grain-elevator [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The data from this registrant study was also used to estimate exposure in this EAD. However, for the grain-elevator commodity fumigation exposure scenarios, the data from the registrant study was combined with that from grain-elevator worker monitoring studies conducted by the National Institutes for Occupational Safety and Health (NIOSH) (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987). The second data source used for the RED was a journal article (Baker, 1992). This article was summarized in the RED which listed the range of "total exposures" and the equivalent TWA's. The article has been summarized in this EAD. However, a more recent and comprehensive study conducted by the same author and a registrant was utilized to estimate exposure for scenarios associated with burrowing pest control [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022].

This EAD contains estimates of phosphine exposure to workers and bystanders associated with the use of the phosphine-generating solids, aluminum phosphide and magnesium phosphide, and cylinderized phosphine gas. These exposure scenarios are for the fumigant applicator, the worker who aerates the structure, workers who assist in application and aeration, the worker who retrieves the spent fumigant, various types of occupational bystanders, and the residential bystander.

PHYSICAL AND CHEMICAL PROPERTIES

Aluminum phosphide and magnesium phosphide are stable solids when dry. However, they both degrade, especially magnesium phosphide, in the presence of atmospheric moisture to generate phosphine gas (Table 5). Phosphine gas, in its pure form, has no odor. However, technical grade phosphine, due to impurities, has an odor resembling garlic or rotting fish (Tomlin, 1997; HDSB, 2011).

Table 5. Physical and Chemical Properties of Aluminum Phosphide, Magnesium Phosphide, and Phosphine

	Aluminum phosphide	Magnesium phosphide	Phosphine
Molecular Formula	AlP	Mg_3P_2	PH_3
Molecular Weight	58	134.9	34
Form	dark grey or yellowish crystals	yellow-green crystals	colorless gas
Vapor Pressure (mmHg at 25°C)	N/A	N/A	2.93×10^4
Melting Point (ºC)	>1000	>750	N/A
Henry's Constant (Pa m^3 mol^{-1})	N/A	N/A	33,269
Specific Gravity/Density	2.85 at 25ºC	2.055	1.18 (air = 1)
Stability	reacts with H_2O	reacts with H_2O	oxidizes to phosphoric acid in the presence of O_2 and oxidizing agents
Flash Point	N/A	N/A	spontaneously ignites in air with an explosion limit of 26.1- 27.1 mg/L
N/A: not applicable			

The PH_3 air concentrations in this EAD are expressed in parts per million (ppm). However, using the ideal gas law, these values may be converted to mg/m^3 using the following formula:

PH_3 air conc. in mg/m^3 = (PH_3 air conc. in ppm) x (molecular weight of PH_3 in g/mol)/24.45 liter-atm/mol

For example, at 1 atmosphere (atm) of pressure and a temperature of 25 degrees C, a phosphine air concentration of 5 ppm is equivalent to 7 mg/m^3.

PHARMACOKINETICS

Dermal Absorption of Phosphine

No studies on the dermal absorption of phosphine, which is a gas with a vapor pressure of 29,300 mmHg at 25ºC (HDSB, 2011), were discovered. However, the ability of phosphine to penetrate other materials suggests that significant percutaneous absorption may occur. The product labels state that phosphine is "highly mobile and given enough time may penetrate seemingly gas-tight materials such as concrete and cinder block". In a study by Wainman, et al., phosphine penetrated hydraulically compressed bales of sheep skins. The authors state that "laboratory trials showed that phosphine penetrates bales quite readily…" The bales contained 9 gas-sampling lines and were fumigated in a chamber over a 7-day period. In the low-dosage experiment, the phosphine air concentration was sampled over this 7-day period and was reported as ranging from 11 to 15 mg · hour/liter. Dividing these values by the 7-day or 168-hr fumigation period yields a concentration range of 66 to 89 µg/liter or 47 to 64 ppm. The specific sampling times during the 7-day fumigation were not listed (Wainman H.E., 1980). In another study,

$^{32}PH_3$ was shown to penetrate into the endosperm and germ fractions of wheat grain. Fumigation of the wheat grain with 8 to 23 ppm $^{32}PH_3$ for 4 to 5 days left ^{32}P residue levels of 3.8 to 7.4 ppm. Twelve and four percent of the residues were in the endosperm and germ fractions, respectively (Tkachuk R., 1972). Although these research studies provide limited information, they suggest that PH_3 may be absorbed percutaneously by the worker.

In spite of the penetrating ability of phosphine, significant percutaneous absorption was not anticipated by the U.S. EPA as stated in the reregistration eligibility decision (RED) document for aluminum and magnesium phosphide. In the dermal absorption section of the RED, the U.S. EPA stated that “Because the route of exposure anticipated for aluminum and magnesium phosphide is inhalation, the Agency does not expect significant dermal exposure. Therefore, dermal absorption studies are not required.” (U.S. EPA, 1998). This sentiment was also found in two other references. In a journal article titled, “Aluminum phosphide ‘Phosfume’ a versatile fumigant”, the authors state that, “the gas has no skin (percutaneous) absorption” (Fachmann I. and Gokhale, M., 1972). However, neither data nor references to studies supporting this statement were found. Also, in a book titled, “PESTICIDES STUDIED IN MAN”, the author states, “The effectiveness of proper gas masks excludes the possibility of significant absorption by the skin” (Hayes W.J.Jr., 1982).

Inhalation Absorption of Phosphine

No quantitative studies were found concerning the absorption of inhaled phosphine. Under these circumstances, for estimating exposure, DPR assumes that 100% of the inhaled compound of interest, in this case phosphine, is absorbed.

Metabolic Fate

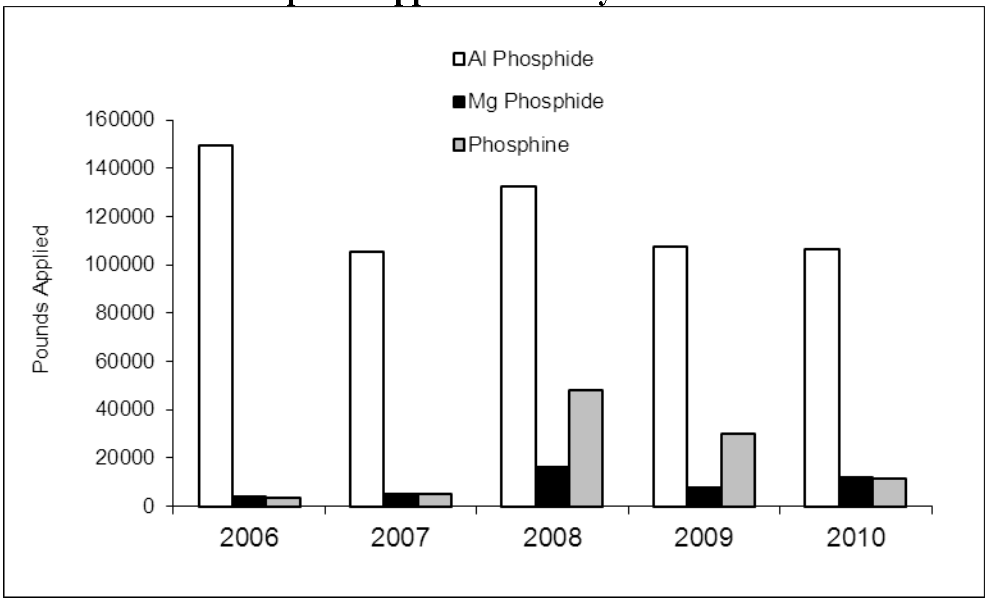
Information on phosphine metabolism is limited. In a study conducted by Lyubimov and Garry, reaction product residues (hypophosphite and phosphite), in ^{32}P-labeled phosphine treated flour were fed to mice. Radiolabeled material was found to persist in the excreta for up to three weeks (Lyubimov and Garry, 2010).

PESTICIDE USE

The Pesticide Use Report (PUR) is a record of all of the pesticides used in the state of California each year. The PUR program was started in 1990 in order to generate a more comprehensive record of pesticide use data. The database provides annual summaries and specific data which can be obtained through the California Pesticide Information Portal (CalPIP) system (CalPIP, 2011). This search engine allows queries of pesticide related data from multiple sources including the PUR database (PUR, 2011).

The total statewide amounts of aluminum phosphide, magnesium phosphide, and phosphine applied annually over multiple years were obtained using CalPIP and the PUR database. The latest 5 years (2006 – 2010) of data from the PUR database show that relatively low amounts of magnesium phosphide were used. In addition, while the annual amounts of aluminum phosphide and magnesium phosphide applied remained relatively constant, the application of phosphine declined from 2008 through 2010 (Figure 1).

Figure 1. Total Pounds of Aluminum Phosphide, Magnesium Phosphide and Phosphine Applied Annually from 2006-2010



The highest use counties varied between the different formulations. Except for 2008, aluminum phosphide was used predominantly in Fresno County. The highest use counties for magnesium phosphide from 2006-10 were Sacramento, Yolo, Fresno, Yolo, and Solano, respectively. The highest-use counties for phosphine from 2006-10 were Kern, Stanislaus, Sacramento, Sacramento, and Stanislaus, respectively (Table 6).

Table 6. Annual Number of Pounds of Al Phosphide, Mg Phosphide, and Phosphine Applied Statewide and in the Highest Use County (2006 – 2010)

Fumigant	Year	Total Pounds Applied (all counties)	Highest Use County
Al Phosphide	2006	149217	Fresno
	2007	105342	Fresno
	2008	132458	Los Angeles
	2009	107502	Fresno
	2010	106234	Fresno
Mg Phosphide	2006	3931	Sacramento
	2007	5284	Yolo
	2008	16086	Fresno
	2009	8008	Yolo
	2010	12216	Solano
Phosphine	2006	3483	Kern
	2007	5341	Stanislaus
	2008	48259	Sacramento
	2009	30194	Sacramento
	2010	11531	Stanislaus

Based upon the PUR data for 2006-10, four types of fumigation were conducted using aluminum phosphide and magnesium phosphide. These types of fumigation are commodity fumigation, space fumigation, spot fumigation, and burrowing pest control fumigation. The types of fumigation were determined via the site/crop selection on the PUR database. Commodity fumigation consisted of the term, "commodity fumigation", as well as more specific terms such as "almond", "barley", or "cabbage". Space fumigation was used to describe the following PUR site terms: "bldg. and structures (non-ag. outdoor)", "commercial storages or warehouses (all or unspec.)", "structural pest control", "commercial, institutional or industrial areas", "animal husbandry premises", "food processing, handling, plant area (all or unspec.)", "feed/food storage areas (unspec.)", and "storage areas and processing equipment". Spot fumigation was used to characterize the following site/crop terms: "farm or agricultural structures and equipment (all or unspecific)", "food marketing, storages or warehouses (all or unspecific)", and "storage areas and processing equipment". Finally, burrowing pest control fumigation was suggested by site/crop terms such as "vertebrate pest control", "animal burrow entrances", and "landscape maintenance". The full site/crop term lists are located in Appendices 1 – 3.

The chemical selection terms "phosphine" or "phosphine gas" on the PUR database were selected to represent cylinderized phosphine gas. Using these terms, phosphine gas was shown to have been used to fumigate commodities such as almonds, pistachios, and rice, and for space, and spot fumigation (e.g., "structural pest control", and "storage areas and processing equipment"). Phosphine was also shown by the PUR database to have potentially been used for burrowing pest control with site/crop terms such as "rights of way" and "landscape maintenance". However, uses reported with these site/crop terms are likely erroneous since no such applications exist on the product labels.

To characterize seasonal use of fumigant, the CalPIP system was used to obtain monthly application amounts of these fumigants for the latest 5 years (2006 - 2010) of PUR data. Seasonal use is defined by DPR as use which is greater than 1 week but significantly less than one year. The length of the season was calculated by summing the number of months having application amounts equal to or greater than 5% of the annual total. For each year, seasonal use was estimated for the county with the greatest number of pounds of fumigant applied. Seasonal use was estimated for structures used to store commodities and undergo space fumigation, and for burrowing pest fumigation. For spot fumigation, the mean amounts of aluminum phosphide, magnesium phosphide, and phosphine applied statewide per year from 2006 – 2010 are 54, 1, and 2 pounds, respectively. These amounts are too low to be considered for the repeated exposures that would suggest seasonal use. Hence, only short-term exposure was estimated for the applicator, aerator, and bystander associated with spot fumigation.

For structures used to store commodities, fumigant use seasons were based upon the types of fumigations anticipated to be used for each structure. For structures used to contain dry flowables (i.e., nuts and grains), such as grain-elevators, farm bins, flat storage facilities, and bulk cars, seasonal use of fumigant was estimated using PUR database site/crop terms for fumigated nuts and grains. In addition, space fumigation may be conducted in these structures. Hence, the PUR database site/crop terms for space fumigation were included when estimating the use season. Two of the PUR database site/crop terms for space fumigation, [i.e.,"bldgs. and structures (non-ag. outdoor)", and "animal husbandry premises"], do not apply for the dry flowable commodity storage structures mentioned above. However, in the highest use county for each year during 2006 - 2010, no aluminum phosphide, magnesium phosphide, or phosphine was applied at these two sites. Hence, they have no effect on the seasonal use estimate. For structures such as the warehouse, ship hold, and box car, which are anticipated to be used to store potentially any of the commodities shown to have been fumigated during 2006 - 2010 (e.g., dry flowables, fruits, vegetables, and grasses), the site/crop terms for all of the commodities treated were used for estimating the use season. In addition, as with the other structures, space fumigation may be conducted. Therefore, the site/crop terms for space fumigation were also utilized for estimating the use season.

For commodity and space fumigation, aluminum phosphide was used in greater amounts than magnesium phosphide, and phosphine. During 2006 – 2010, according to the PUR database, 217,121 lbs. of aluminum phosphide were applied statewide for commodity fumigation of nuts and grains. This is substantially higher than the 29,849 lbs. of magnesium phosphide and 76,115 lbs. of cylinderized phosphine gas applied for these commodities statewide over this same period. For fumigation of all commodities including nuts and grains, 500,807 lbs., 77,801 lbs., and 30,780 lbs. of aluminum phosphide, phosphine, and magnesium phosphide, respectively, were applied during 2006 – 2010. For space fumigation, 30,470 lbs., 16,712 lbs., and 1159 lbs. of aluminum phosphide, phosphine, and magnesium phosphide, respectively, were applied from 2006-

2010. For burrowing pest fumigation, 237,750 lbs., and 443 lbs. of aluminum phosphide and magnesium phosphide were applied during 2006 – 2010. Cylinderized phosphine gas is not used for burrowing pest fumigation.

In all cases, aluminum phosphide was the fumigant used in the greatest amounts. Hence, the use season for this fumigant was utilized to estimate seasonal exposure in this EAD. The estimated use season for dry-flowable commodities, and space fumigation is 8 months (i.e., January, and April – October). The use season for all commodities fumigated, and space fumigation is also 8 months (i.e., January, March – July, and September – October). Finally, the use season for burrowing pest fumigation is 6 months (March - April, and August – November).

In addition to estimating the seasonal use of aluminum phosphide, the PUR database was utilized to estimate the seasonal application rates for this AI. The seasonal application rate was used in lieu of the product label maximum application rate for estimating seasonal exposure air concentrations. The data retrieved from the PUR database for 2006 - 2010 were expressed as the number of pounds of chemical applied ("sum lbs chemical"), the site or crop treated ("site name"), the amount treated ("sum amt treated"), and the units for the amount of commodity, space, or acreage treated ("unit treated description"). The seasonal application rate was estimated using these results for space fumigation and the fumigation of dry-flowable commodities (i.e., nuts and grains), in farm bins, flat storage facilities, ship holds of bulk dry cargo vessels, bulk cars, and in the upright bins of grain-elevators. The seasonal application rate was also estimated for the fumigation of all commodities treated and for space fumigations in structures such as the warehouse, mill, food processing plant, ship container, barge, bunker, and box car. Finally, the seasonal use application rate was estimated for burrowing pest fumigation.

Multiple types of units for the amount of commodity or space treated were provided by the PUR database. These labels were "misc. units (eg. bins, treeholes, pallets)", "tons", "pounds", "acres", "square feet", "unknown", "cubic feet", and "thousand cubic feet". The application rates listed on the product labels are in grams/cubic foot or grams/bushel, which can be converted to grams/cubic foot. Hence, only the amounts of commodity treated which were listed in either "cubic feet" or "thousand cubic feet" were used to estimate the seasonal application rate. For dry flowable commodities (nuts and grains) and space fumigation, 24% of the results were expressed as cubic feet or thousand cubic feet. Seventy-three percent of the application rates calculated from these data is at or below the product label maximum (0.145 grams/cubic foot). The other 27% were above the product label maximum application rate. Hence, these data were assumed to be erroneous and were not used to estimate the seasonal application rate. In addition, the pounds applied for the site/crop terms, "bldgs. and structures (non-ag. outdoor)", and "animal husbandry premises" were omitted for estimating the seasonal use application rate since they're unrelated to structures used to store nuts and grains. Based on these criteria, the mean aluminum phosphide application rate for dry flowable commodity fumigation and space fumigation for the years 2006 – 2010 is 0.06 grams/cubic foot. The mean aluminum phosphide application rate for all commodities treated and space fumigations combined for 2006 – 2010 is also 0.06 grams/cubic foot. Twenty-six percent of the data for the amount treated were expressed in “cubic feet” or “thousand cubic feet”. Of this data, 81% of the calculated application rates were below or equal to the product label maximum.

The seasonal use application rate for burrowing pest fumigation was estimated in units of pounds of aluminum phosphide applied per acre treated. Multiple types of units for the amounts of area treated for burrowing pest fumigation were provided by the PUR database. These labels were “misc. units (e.g., bins, treeholes, pallets)”, “pounds”, “acres”, “square feet”, “unknown”, and “cubic feet”. The only potentially useable data were those labeled in acres or square feet. Eighty-five percent of the data retrieved from the PUR database for burrowing pest fumigation were in acres while 14.3 % were in square feet. However, in terms of total acreage treated during 2006 – 2010 (i.e., 25,698 acres), 0.01% of the acreage or 2 acres was labeled in “square feet” while 99.99% of the acreage treated (i.e., 25,696 acres) was labeled in “acres”. Conversion of the “square feet” data to acres, generated relatively high application rates which ranged from 0.2 to 60.5 lbs of aluminum phosphide applied per acre. The mean of these application rates is 18.7 lbs. per acre. In contrast, the mean application rate of the data originally expressed in acres is 0.2 lbs./acre.

While this rate information derived from the PUR database is informative, it lacks the specificity required for normalizing the air concentration data in the exposure study to a seasonal application rate. Although, some of the rates listed in the exposure study were in lbs. of AI applied per acre, the only useful application rates were those expressed as the number of tablets applied by each worker per day. Only these rates could be correlated with the specific air concentration values used to assess short-term exposures. Hence, the seasonal exposures were estimated using the same application rate as that used to estimate the short-term exposures.

PRODUCT LABEL SAFETY INFORMATION

The signal word for aluminum phosphide, magnesium phosphide, and phosphine is “Danger”, which is used for Toxicity Category 1 pesticides (40 CFR 156.64). Product labels for all three active ingredients contain the words “Restricted Use Pesticide”, and, as a result, must be applied by or under the direct supervision of a certified applicator (40 CFR 152.175). They are also listed as “Restricted Materials”, in California (3 CCR 6400). In the state of California, a handler using a restricted material must be certified by DPR as having had specific training for pesticide handling and usage. Also, the user must obtain a permit from the County Agricultural Commissioner, who assesses the potential health and environmental effects of the application (DPR, 2001).

Personal Protective Equipment (PPE)

<u>Aluminum Phosphide and Magnesium Phosphide</u>

The product labels have PPE requirements to reduce dermal and inhalation exposures. Each product label contains instructions for the handler to wear dry gloves made of cotton or “other material” if contact with the product is “likely”. Respiratory protection is required if the air concentration of phosphine is unknown and, as stated on some product labels, if the permissible exposure limits are exceeded. A NIOSH/MSHA approved, full-face gas mask-phosphine canister combination may be used with phosphine air concentrations up to 15 ppm. It may also be used for “escape”. However, as stated on the product labels, if the phosphine levels exceed 15 ppm or are unknown, a NIOSH/MSHA approved self-contained breathing apparatus (SCBA) must be worn. The assigned protection factor (APF) for this type of device and the SCBA for phosphine levels that are above 15 ppm or are unknown is 10,000 (NIOSH, 2010). Two types of modes exist for the SCBA, the demand mode and the pressure-demand mode. The demand mode has a maximum use concentration (MUC) of 15 ppm. This value is obtained by multiplying OSHA’s APF of 50 with the 8-hr TWA PEL (0.3 ppm) to get the MUC of 15 ppm (Beauvais, 2011). However, for phosphine concentrations exceeding 15 ppm, the pressure-demand mode, with a MUC of 3000 ppm would be required. Certain product labels state that a SCBA must be worn during “entry into sites that are under fumigation” if the phosphine concentration is unknown or exceeds the short-term exposure level (STEL) of 1 ppm for 15 minutes. Moreover, as stated on some of the product labels, if monitoring equipment is not available and the application must be made from within the structure, an approved canister respirator must be worn.

DPR’s assigned protection factors for respiratory protection are derived from OSHA’s assigned protection factors. For example, the OSHA protection factor assigned for the full face gas mask-phosphine canister combination is 50. This factor is equivalent to the DPR assigned protection factor of 98%. The DPR factor is derived from the OSHA factor by dividing 1 by the OSHA protection factor, in this case 50, which generates a value of 0.02. This value is the proportion of phosphine which penetrates the respirator. This value is then subtracted from 1 to get 0.98. This value is then multiplied by 100% to get 98% (Beauvais, 2011). Using this approach, DPR’s assigned protection factor for the SCBA in pressure-demand mode, which has an OSHA protection factor of 10,000, is 99.99%.

For indoor applications, all of the product labels contain the requirement that an approved full-face gas mask-phosphine canister combination or SCBA or its equivalent to be available within the structure being fumigated.

For outdoor applications, the requirements vary depending upon the brand of fumigant. Some product labels contain the requirement that respiratory protection be available for applications from outside the area to be fumigated. Other labels contain language stating that respiratory protection need not be available for applications from outside the area to be fumigated if exposures do not exceed the permitted exposure limits.

Cylinderized Phosphine

As with aluminum phosphide and magnesium phosphide the two product labels for cylinderized phosphine gas have PPE requirements. When applying phosphine from the pressurized gas cylinder, the worker must wear “leather or leather faced gloves”. In addition, NIOSH/MSHA approved respiratory protection must be worn during exposure to phosphine concentrations in excess of permitted limits or when concentrations are unknown. A SCBA must be worn when “troubleshooting for leaks”, if the phosphine concentration is unknown or exceeds the STEL of 1 ppm for 15 minutes and/or the carbon dioxide STEL of 30,000 ppm for 15 minutes (carbon dioxide is applied along with the phosphine gas to prevent explosions). Respiratory protection must be available at the site of application, including an adequate number of SCBA devices operated in pressure-demand mode. Each cylinderized phosphine product label contains a table showing NIOSH-recommended respiratory protection (Table 7).

Table 7. NIOSH-Recommended Respiratory Protection for Workers Exposed to Phosphine Gas

Phosphine (ppm)	Minimum Respiratory Protection
0.3 – 3	Supplied-air respirator
7.5 or less	Supplied-air respirator operated in a continuous-flow mode
15 or less	Self-contained breathing apparatus with full facepiece or supplied-air respirator with a full facepiece, or air-purifying full facepiece respirator (gas mask) with a chin-style front- or back-mounted canister
50 or less	Supplied-air respirator equipped with a full facepiece and operated in pressure-demand mode or SCBA with full-facepiece and operated in a pressure-demand mode

Physical and Chemical Hazards

According to the product labels, phosphine is explosive and corrosive. At air concentrations above its lower flammable limit of 1.8% v/v, the gas may spontaneously ignite. For the phosphine generators (i.e. aluminum phosphide and magnesium phosphide), spent or partially spent fumigant should not be confined but allowed to aerate to promote dilution. For pressurized phosphine gas, the air concentrations inside of the fumigated structure must be constantly monitored in order to prevent buildup to explosive levels. Moreover, the phosphine must be diluted with carbon dioxide or forced air during application to reduce risk of explosion. Phosphine can corrode certain metals such as brass, copper, gold, and silver. Therefore, electric motors, smoke detectors, brass sprinkler heads, batteries, computers, etc. should be sealed from the phosphine gas or removed from the structure prior to fumigation.

California Requirements

Numerous titles and sections in the California Code of Regulations apply to phosphine and the phosphine generators, aluminum phosphide and magnesium phosphide. Under Title 3 (Food and Agriculture), 5 sections refer to fumigation in general. In Section 6400 all three products are listed as “restricted materials”, which is defined as pesticides with the potential to cause injury to people, crops, or the environment (DPR, 1997). In Section 6860, phosphine is listed as a toxic air contaminant which is defined as an air pollutant that may cause or contribute to increases in serious illness or death or that may pose a present or potential hazard to human health. The Toxic Air Contaminant Act focuses on “identifying, evaluating, and controlling pollutants in ambient community air” (DPR, 2012a). Section 6630 contains rules for labeling pesticide equipment. Section 6780 contains procedures for preventing worker exposures to fumigant concentrations above the stated limits (e.g. permissible exposure level). Section 6782 contains the proper procedures for fumigating enclosed spaces such as chambers or boxcars.

Title 8 (Industrial Relations), has 3 sections for fumigants. Section 5221 contains general safety procedures for fumigation. Section 5222 has safety rules for fumigating vaults and chambers while section 5223 contains safety procedures for fumigating buildings or rooms other than vaults and chambers.

Title 16 (Professional and Vocational Regulations) has 7 sections for fumigants. Section 1970 contains requirements for generating and maintaining records of fumigations. A definition of an “enclosed space” is in Section 1970.1, while Section 1970.3 contains entry restriction requirements for fumigated structures. Section 1970.4 has instructions for the “pesticide disclosure document” which provides fumigant and application information to “occupants” or the “designated agent” of a structure to be fumigated. Section 1970.6 has rules for preventing movement of fumigant from a treated structure into adjacent structures where bystanders could be exposed. Section 1971 contains rules for a fumigation safety kit containing respirators, first aid instructions, manufacturer’s instructions for the fumigant being applied, and air monitoring equipment. Finally, Section 1974 has instructions for posting warning signs.

Title 26 (Toxics) has 5 sections for fumigants. Sections 16-1970, 16-1970.1, 16-1970.3, and 16-1970.4 are redundant and contain the same information as Title 16, Sections 1970, 1970.1, 1970.3, and 1970.4, respectively. Section 16-1970.5 has a definition for the aeration step of the fumigation process.

REPORTED ILLNESSES

Following the investigation of a potential case of pesticide poisoning, the County Agricultural Commissioner files a report, which is logged in the California Pesticide Illness Surveillance Program (PISP) database. Using the California Pesticide Illness Query (CalPIQ) search engine, for the latest 5 years of data (2005-2009), there are 10 reported cases of illness associated with aluminum phosphide, no cases associated with magnesium phosphide, and 27 cases associated with cylinderized phosphine. Exposure is described as being a “definite”, “probable”, or “possible” cause of each reported illness. As stated on the CalPIQ website, “A **definite** relationship indicates that both physical and medical evidence document exposure and consequent health effects. A **probable** relationship indicates that limited or circumstantial evidence supports a relationship to pesticide exposure. A **possible** relationship indicates that health effects correspond generally to the reported exposure, but evidence is not available to support a relationship” (CalPIQ, 2011).

Ten cases of phosphine exposure are listed for “aluminum phosphide” in the PISP database from 2005-2009. Six of the cases occurred in 2005. The first case (case number 253) occurred in Fresno County. In this case, a feed mill worker located 2 floors below a fumigated and aerated feed bin was reported as smelling a garlic odor prior to suffering from a headache, abdominal pain, dizziness, and painful teeth. Other workers in the mill were reported as smelling the same odor. Phosphine exposure was reported as being "probable". In the second case (case number 601), also in Fresno County, an almond processing plant worker who sorted the almonds developed irritation in the left eye upon noticing a white powder. The report stated that the almonds are fumigated prior to being processed and the spent fumigant powder is removed in envelopes. Phosphine exposure in this case was reported as being "possible". The next three cases listed (case numbers 1307-1309) were due to a single incident where 3 individuals broke into a fumigating box car and closed all of the openings in order to avoid detection. All three individuals died. Phosphine exposure was reported as being "definite" in all three cases. In the fourth case (case number 1310), an intensive care nurse who treated one of the individuals developed shortness of breath, a burning sensation around the neck, and welts on the arms. Phosphine exposure in this case was reported as being "possible". These 4 cases occurred in Riverside County. The next case (case number 613) occurred in San Bernardino County in 2006 and consisted of a warehouse forklift driver who was reported to have inhaled fumes from improperly disposed of spent fumigant that had ignited. The driver was reported to have experienced pain in the eyes, stomach, and head. Phosphine exposure was listed as being "probable". One case (case number 844) occurred in 2007 in Merced County. In this case, a trainer without the proper qualifications instructed an inexperienced worker to fumigate sacks of almonds. The worker did not wear PPE and became ill after a few hours. The worker's symptoms included nausea, vomiting, headache, fatigue, and a chemical taste in mouth. The last two cases in the report (case numbers 412 and 1031) occurred in 2009 in Merced and Fresno Counties, respectively. In case number 412, a field worker became ill (i.e., nausea and vomiting), on the 2nd day of applying aluminum phosphide to animal burrows. The worker was reported as not being a certified applicator. Phosphine exposure in this case was reported as being "possible". In case number 1031, an individual renting a house applied aluminum phosphide pellets to a squirrel hole adjacent to the garage and gas meter. A few hours later, the occupants of the house experienced coughing, dizziness, and a "sensation of fluid in the lungs". Phosphine exposure in this case was reported as being "probable" (CalPIQ, 2011).

For the years 2005-2009, 27 potential cases of phosphine exposure, due to the use of "phosphine" are listed in the PISP database. In 2007 in San Joaquin County, a bulk storage operator was reported as being exposed to phosphine gas escaping from a fumigated rail car with a faulty hatch cover. The operator was not wearing a respirator. The worker experienced symptoms including fatigue and skin irritation several hours after the incident (case number 703). In 2007 in Kern County, twenty three of the cases (case numbers 1229, 1231, 1234-1240, 1242-1245, 1446, 1449, 1453, 1456, 1459, 1464-1466, and 1478-1479), occurred in a single incident at an almond processing plant where the fumigant was applied using an illegal method. According to the label, the cylinderized phosphine is supposed to be applied from outside of the facility being fumigated. However, in this case, the applicators placed the cylinder of gas in the plant and then opened the valve. Following "aeration", the plant workers returned. During the application, the phosphine fumigant had penetrated into the cold room which was not monitored. Upon opening the doors, 23 workers complained of a strong odor and subsequently experienced symptoms including headache, nausea, and dizziness. Phosphine exposure in twenty-one of the cases was reported as being probable and, in 2 of the cases, as being possible. In 2008 in Butte County, workers entered an unlabeled bin containing walnuts undergoing fumigation. The warning placards were reported as being torn off by the weather prior to the workers entering the bin. One of the workers experienced symptoms including "burning throat pain", "chest constriction", and nausea. An applicator measured levels within the bin and found levels to be "high". Phosphine exposure in this case was reported as being "probable". The case number for this incident is 45. Another case (case number 894), in 2008 in Stanislaus County consisted of a worker sorting almonds in a "fogged" warehouse who experienced symptoms 2 days after the treatment. The symptoms included difficulty breathing, nausea, and a headache. However, in addition to phosphine, the pesticide, DDVP, was listed as the possible culprit. Phosphine exposure in this case was reported as being "possible". Finally, in 2008 in Kern County, a plant supervisor instructed a worker sorting almonds to place a fumigation "probe" into piles of almonds covered by tarpaulins. The worker was reported as having "smelled the fumigant", and experienced symptoms including nausea, vomiting, stomach pain, cramps, sweating, and weakness. Phosphine exposure in this case was reported as being "probable" (case number 1071) (CalPIQ, 2011).

EXPOSURE ASSESSMENT

Exposure estimates are provided for exposure scenarios representing the fumigant applicator, occupational bystander, and residential bystander. For each scenario, estimates are provided for short-term (defined in this EAD as the work-shift exposure each day for up to one week), seasonal, annual, and lifetime exposures. Seasonal exposure is defined as a period of exposure lasting for more than a week but substantially less than a year. Annual exposure is defined as seasonal exposure amortized over the entire year.

When data were available, the highest work shift air concentration was used to estimate the short-term exposure air concentration. Frequently, DPR uses the 95th percentile of the population which is assumed to be lognormally distributed. However, this approach was not used in this EAD since the 95th percentile values have trends which were the opposite of the respective means (i.e., the mean of one data set is lower than that of the other set while the estimated 95th percentile is higher). In addition, the data sets for some scenarios (e.g., 1 or 2 samples) don't have enough data to generate a 95th percentile of the population estimate. Since comparison of the these data sets is crucial to generating meaningful exposure estimates, the procedure for estimating the 95th percentile of the population which is assumed to be logarithmic was not used in this EAD. Instead, for each scenario, the highest measured air concentration was utilized to estimate short-term exposure. This air concentration was corrected for recovery if the field fortification study yielded a sample recovery of less than 90%. The air concentration was then multiplied by the product label maximum application rate and then divided by the application rate used in the exposure study (Powell, 2003).

The arithmetic mean of the air concentration exposure data was used to estimate seasonal exposure. The mean value of the exposure data incorporates all of the data, including the highest values. Other measures of the average, such as the median or geometric mean are better indicators of the center of the distribution. However, DPR is concerned with the expected magnitude of exposure. Extremely high daily exposures are not common (i.e., DPR assumes that with increased exposure duration, repeated daily exposure at the upper-bound level is unlikely), but do occur, and the arithmetic mean weighs these exposures in proportion to their probability. In contrast, the geometric mean gives decreasing weight as the value of the exposure data increases and the median does not give any weight to extreme exposure values. DPR believes that the mean daily exposure of a group of individuals observed in a short-term study is the best available estimate of the mean daily exposure of a given individual over a season, year, or lifetime (Powell, 2003). The air concentration data used to estimate seasonal exposure were corrected for recovery if the field fortification study yielded a sample recovery of less than 90%. The air concentration data were then multiplied by the estimated seasonal application rate for aluminum phosphide and divided by the application rate used in the exposure study.

According to the product labels, for the following structures, two general approaches exist for the application of phosphine fumigant. The applicator can enter the structure to apply the fumigant or the fumigant can be applied via a phosphine generator or dispensing device from outside of the structure. The studies described below contain air concentration data generated via the use of fumigant formulations which are applied indoors by the handler. No personal TWA breathing-zone data were available for the cylinderized gas and granular formulations, which are applied from outside of the sealed structure via a dispensing apparatus (i.e., gas cylinders, or, in the case of the granular formulation, a phosphine generator). As a result, the exposure estimates generated for the applicator in the studies below were chosen to act as surrogate estimates for the applicator using granular or cylinderized gas formulations. In addition, the aerator and bystander exposure estimates generated below were selected to act as surrogate estimates for the aerators and bystanders associated with fumigation using granular or cylinderized gas formulations.

Commodity Fumigation in Concrete Upright Bins of Grain-Elevators

The grain-elevator is used to condition and store grain. The grain (e.g. corn, soybean, or wheat), is delivered to the elevator via truck, train, or barge and is transferred up to the top of the elevator and into concrete upright bins or silos via the use of bucket elevators or enclosed conveyor belt systems called grain legs. The grain can also be transferred from one concrete upright bin to another within the grain elevator in a process called "turning". The elevator owners buy grain from farmers or the owners of other grain-elevators and "blend" the grain to adjust the grain properties, such as moisture level, to the proper specifications for the intended use. The grain is then sold to other grain-elevator owners or food processor companies.

The grain-elevator complex consists of several structures: the concrete upright bins or silos, the office building, and the headhouse which contains all of the floors used for processing the grain. Each floor or level of the headhouse serves a specific function within the grain-elevator. The top level of the headhouse is called the "head area" which is used for maintenance and repair of the elevator. The next floor below that is the "scale floor" where all grain coming into or going out of the elevator is weighed. From this floor, the weighed grain is transferred to the “distributor floor” where the grain is directed via chutes to the “gallery”, “bin deck”, “bin floor”, or “tripper floor”. From this floor the grain is further directed to either the desired long-term storage bin(s) via conveyor belts, and “trippers” or to a hopper or temporary concrete upright bin from which it is transferred into a truck or rail car. In some cases, the grain may also be sent to the “transfer floor” which consists of horizontal open conveyor-belts that transfer the grain outside of the headhouse and ultimately to other nearby storage bins. In the basement of the headhouse, also known as the “tunnels” or “tank floor”, the grain from each concrete upright bin can be released through an opening or hopper at the bottom of the bin and transported via conveyor systems called “grain legs” back up to the scale floor (NIOSH Composite Report, 1987).

During the 1980’s, phosphine levels in the breathing-zones of workers within grain-elevators undergoing commodity fumigation were measured in separate studies by a registrant task-force [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015] and by the National Institute for Occupational Safety and Health (NIOSH) (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987). The PH_3 breathing-zone air concentrations of workers in four grain-elevators were monitored in the NIOSH study while those of workers in three grain-elevators were monitored in the registrant study. Of the three AI’s (i.e., magnesium phosphide, aluminum phosphide, and cylinderized phosphine gas), only aluminum phosphide (pellets or tablets) was used to fumigate grain in the concrete upright bins of the elevators in these investigations. According to the product labels, commodity fumigation within the grain elevator may also be conducted using aluminum phosphide tablets packaged in bags, blister packs, or polymeric fleece, or magnesium phosphide packaged in bags or in tablet form. However, these formulations were not utilized in these studies. Hence, the phosphine air concentration data obtained for the aluminum phosphide tablet or pellet applications were selected to act as surrogate air concentrations for these other formulations.

Aluminum phosphide fumigant was applied to the grain in the commodity fumigation studies via two different methods. The first method consisted of manually adding the fumigant pellets or tablets by hand to the grain as it travels through the grain leg. The other method consisted of using an “auto-dispenser” which drops the tablets or pellets at a specified rate into the grain as it passes by on a conveyor belt. The handler may have to repeatedly fill the reservoir of the auto-dispenser during the application. Following the application, the handler may also have to empty the dispenser of any remaining fumigant tablets or pellets (NIOSH Composite Report, 1987). Both application methods are the methods currently listed on product labels for tablet and pellet formulations for commodity fumigation in upright bins in grain elevators.

Two types of personal air samples were obtained from the breathing-zones of the fumigant applicator and occupational bystander. The first type of sample had a relatively long sampling period and was used to calculate the time-weighted-average (TWA) PH_3 breathing-zone air concentrations for the handlers applying the fumigant and the occupational bystanders (workers who do not directly contact the fumigant or the fumigant container). These samples were obtained in three grain-elevators by the registrant task force and in four grain-elevators by the NIOSH investigators. The mean sampling periods used in the registrant and NIOSH studies were 3 and 6.8 hours, respectively. The TWA air concentrations in the registrant and NIOSH studies were measured using NIOSH method number S332. This technique consists of pumping a known volume of air from the breathing-zone or the ambient air over a silica column coated with mercuric cyanide using a personal sampling pump. The phosphorous of the adsorbed PH_3 is then extracted from the column and oxidized to phosphate using hot acidic permanganate solution. The phosphate of the sample is then converted to a phosphomolybdate complex. The phosphomolybdate complex is then reduced and measured via light absorption at 625 nm using a spectrophotometer (NIOSH, Composite Report, 1987). For the TWA personal air sample data, air concentration values from samples identified as coming from columns that had "breakthrough" (i.e., significant amounts of sample had broken through the 1st compartment of the column media), or variable flow rates due to sampling pump issues were not used to estimate exposure. Of the 141 personal air samples taken from both the registrant and NIOSH studies, 8 samples were voided (i.e., 6% of the total), with 6 samples being voided due to breakthrough and 2 samples being voided due to variable flow rates.

The second type of sample, obtained only in the NIOSH studies, was the "instantaneous" air sample with a sampling period of up to 5 minutes in length. These samples were taken from the applicators' breathing-zones while they were filling and emptying fumigant auto-dispensers or manually adding fumigant to the grain. Filling or emptying the auto-dispenser was stated to take about 5 minutes and occur up to 7 times/day. The phosphine breathing-zone air concentrations, in the absence of respiratory protection, ranged from 0.1 to 52 ppm with a mean value of 11.3 ppm. Manual application of fumigant to the dry-flowable commodity was stated to take approximately 1 minute and occur up to 20 times/day. The two samples taken of breathing-zone air concentrations were 0.2 to 0.6 ppm. These air concentrations would exist in the absence of respiratory protection. The instantaneous sampling technique consisted of pumping air from the breathing-zone into a bag made of Tedlar® or aluminized polyester using a personal air-sampling pump. The air within the bag was then analyzed for PH_3 using a gas-chromatograph equipped with a photoionization source and detector. The NIOSH study also included sampling data of various areas within the grain-elevators. Due to the extremely short exposure periods (i.e., ~5 minutes), the instantaneous samples were not directly used to estimate work shift exposures. However, these episodic exposures would have been incorporated into the TWA samples which were also collected from the workers and were used for estimating exposure (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, and NIOSH Report 149.18, 1987).

The method limit of detection (LOD) is a measure of the sensitivity of the analytical method used to measure the analyte of interest, in this case $PH_{3,}$ within the sample. For the NIOSH method S332, the LOD is stated as being 0.19 µg PH_3 which is equivalent to approximately 9 ppb for a 16 liter sample. The LOD was "determined from twice the standard deviation for the absorbance of six blank treated silica gel tubes". The instantaneous sampling method utilized in the NIOSH study was reported as having a

LOD ranging from 20 to 60 ppb (NIOSH Composite Report, 1987, and NIOSH Report 149.12, 1986).

For estimating exposure, the numerous TWA personal sampling data from both the registrant and NIOSH studies were consolidated into replicates for the applicator and occupational bystander. A replicate represents the sample or the arithmetic mean of the samples taken from the breathing-zone of one worker/work-shift. According to this definition, in the registrant study, a total of 10 applicator replicates and 23 occupational bystander replicates were generated during application and fumigation at the three grain-elevators. In the NIOSH study, a total of 10 applicator replicates and 15 occupational bystander replicates were generated during application and fumigation at the four grain-elevators. The registrant and NIOSH studies also contained occupational bystander scenario data that were taken post-application but during fumigation of the commodity. For the registrant study, a total of 18 replicates were taken for this scenario while one replicate was generated in the NIOSH study. In addition to post-application/fumigation samples, breathing-zone samples were taken from workers who transferred aerated grain from one bin to another or from the grain-elevator to a truck or rail car or vice versa. Other duties carried out during the grain-transfer were maintenance, and working in the office outside of the grain-elevator. Ten replicates were generated in the registrant study for this "post-aeration" occupational bystander scenario. None were generated in the NIOSH study.

The data in the registrant and NIOSH grain-elevator studies suggest that the applicator operating the auto-dispenser was exposed to greater levels of PH_3 than the applicator manually adding the fumigant to the grain. Twenty-six samples were taken for the applicator using the auto-dispenser while 9 samples were taken for the manual applicator. The mean sampling time for the auto-dispenser samples is 335 minutes while that for the manual applicator studies is 219 minutes. The mean application rate used in the auto-dispenser studies is 0.05 grams/bushel while that used in the manual application studies is 0.04 grams/bushel. The mean of the measured air concentrations for the applicator using the auto-dispenser is 0.52 ppm. The mean of the measured air concentrations for the manual applicator, adjusted for the relatively higher application rate used in the auto-dispenser studies, is 0.05 ppm. Finally, the highest measured air concentration taken in the auto-dispenser studies is 1.67 ppm while that for the manual applicator studies is 0.13 ppm. In all cases, for estimating exposure, the measured sample PH_3 concentrations which were below the LOD were made equal to ½ of the LOD.

Field-fortifications for the TWA samples were conducted in all of the registrant and one of the NIOSH grain-elevator studies. The field-fortification method used by the registrant task-force consisted of evacuating a bag of nitrogen gas containing 0.6 ppm of PH_3 through a sampling column and sending the column to a lab for analysis. All three grain-elevator studies contained field-fortification samples. The mean recoveries were 99, 74, and 95% for the breathing-zone samples taken during application and 90, 100, and 100% for the post-application breathing-zone samples. The mean sample recoveries for the field-fortification experiments conducted during the post-aeration studies were 88 and 80% [Phosphine Worker Exposure, Degesch America (2002) Registration Package

51882-015]. For estimating exposure, if the field-fortification recovery was ≥ 90%, then the breathing-zone samples were not corrected for recovery. Only one of the four sites in the NIOSH study contained information on field-fortification methods and data. At this site, two field-fortification samples were generated via a method similar to that used by the registrants. However, the concentration and complete make-up of the standardized phosphine gas was not mentioned. The mean recovery of these two field-fortification samples was 84%. Samples in this study were corrected for this recovery. Since no field-fortification data were present in the three other sites, the samples from those studies were also corrected for 84% sample recovery (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, and NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987).

No background PH_3 air concentration data were available for the TWA samples in either the registrant or NIOSH studies. The registrants generated background samples via opening the sampling tube and then immediately sealing the tube for analysis. These samples were not used however, since they generated a false-positive signal that increased with increasing storage time [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. This instability was not present in their field-fortification samples. No background sample data were available for the NIOSH studies (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, and NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987). Due to the lack of background data, sample correction for background PH_3 levels for the TWA samples was not carried out in either the registrant or NIOSH studies.

Background PH_3 data were available for some of the instantaneous samples obtained in the NIOSH studies. Two of the three aforementioned studies of the grain-elevators undergoing commodity fumigation via the auto-dispenser method had background samples taken from outside of the elevator (NIOSH Report 149.10, 1986, and NIOSH Report 149.18, 1987). For these two studies, the breathing-zone samples taken while filling or emptying the auto-dispenser were corrected for background. The one NIOSH study of the grain-elevator undergoing commodity fumigation via the manual application method did not have any background sampling data. Hence, the samples were not corrected for background levels of PH_3 (NIOSH Report 149.12, 1986).

Estimating PH_3 Exposure to the Applicator and Occupational Bystander

For estimating applicator exposure, the replicates from the registrant and NIOSH studies were consolidated according to the application method (i.e., manual vs. auto-dispenser) used at the study site. As mentioned earlier, the mean sampling time for the auto-dispenser applicator samples is 335 minutes while that for the manual applicator studies is 219 minutes. The PH_3 air concentrations obtained for these sample periods are assumed to exist for the entire work-shift. For the manual and auto-dispenser application methods, the overall means of the data sets of the PH_3 breathing-zone air concentrations (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), are 0.07 and 0.8 ppm, respectively. The highest values of the data sets of the PH_3 breathing-zone air concentrations for the manual and auto-dispenser application methods were used to estimate short-term exposure. The air concentrations were corrected for recovery if the mean recovery of the study was < 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. The highest of these adjusted values for the manual and auto-dispenser application methods are 0.6 and 5.8 ppm, respectively (Table 8).

Table 8. Summary of Time-Weighted-Average Breathing-Zone Air Monitoring Data for Handlers Conducting Auto-Dispenser or Manual Application of Aluminum Phosphide (Tablet or Pellet Formulations) in Grain Elevators

Data Source [a]	Application Method [b]	Mean Sampling Period (hr) [c]	Number of Replicates [d]	Mean Air Concentration (ppm) [e]	Highest Work Shift Air Concentration of Data Set (ppm) [f]
Registrant	auto-dispenser	3	4	auto-dispenser 0.8	auto-dispenser 5.8
Registrant	auto-dispenser	3	3		
NIOSH	auto-dispenser	7.7	2		
NIOSH	auto-dispenser	6	3		
NIOSH	auto-dispenser	8	3		
Registrant	manual application	3	3	manual application 0.07	manual application 0.6
NIOSH	manual application	7	1		

[a] Registrant: studies conducted on PH_3 exposure to workers and bystanders in grain elevators. [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. NIOSH: studies conducted by the National Institutes of Occupational Safety and Health on PH_3 exposure to workers and bystanders in grain elevators (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, and NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987).

[b] Auto-dispenser application: Tablets or pellets are loaded into motorized auto-dispenser which drops tablets into grain passing underneath unit on conveyer belt. Manual application: fumigant is manually poured via an access door into grain flowing through the grain leg.

[c] Mean amount of time that air in breathing-zone of applicator sampled for PH_3. The mean number of hours for the work-shift is 9.7.

[d] A replicate represents the work-shift (12 and 9.7 hrs TWA for short-term and intermediate exposure estimates, respectively) breathing-zone PH_3 air concentration for one worker. One or more breathing-zone air samples may be generated for a worker during the work shift. If more than one sample was generated, then the mean of the samples was taken to represent the worker's exposure for the work shift. The total sampling period for the worker was shorter than the estimated work shift period of 12 hours for the short-term exposure estimate or 9.7 hours for the intermediate-term estimates. However, the sample air concentration or mean of the sample air concentrations was assumed to be equal to the breathing-zone air concentration for the entire work shift.

[e] The overall mean air concentration of all TWA air concentration data (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), generated in the studies shown for the handler using the auto-dispenser or manual application methods. The mean air concentrations were used to estimate intermediate-term exposure.

[f] The highest replicate values were obtained from air concentration data which were corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study. These peak values were used to estimate short-term exposure to PH_3. The auto-dispenser applicator scenario has 15 replicates that range from 0.2 to 5.8 ppm. The manual applicator scenario has 4 replicates that range from 0.01 to 0.6 ppm.

For estimating occupational bystander exposure, the replicates were organized according to the location of the bystander during the work-shift. In a study by Reed, the data suggest that the location of the worker influences exposure (Reed C., 2001). The author measured PH_3 air concentrations, using electrochemical detectors, at various locations in 24 grain-elevators undergoing commodity fumigation. The results suggest that during fumigation, the floors of the grain-elevator which are located at or above the bin-top openings, such as the gallery (also known as the distributor floor, bin floor, or tripper floor), and the scale floor have relatively higher phosphine air concentrations than the work areas of the elevator which are below the bin-top area such as the ground-level work areas and the basement or tunnels. In the study, 27% of the air sampling results which were taken in areas at or above the tops of the bins was equal to 0 ppm. However, at ground level, 72% of the air sampling results is equal to 0 ppm. Moreover, based upon the air samples taken in the study, the author stated that the air in the bin-top level locations was 14 times more likely to contain PH_3 concentrations in excess of 3 ppm than the air in worker areas at ground level. This trend was reported by the author to also exist in the previously discussed grain-elevator PH_3 exposure studies carried out by the registrants. The author also stated that location influenced worker PH_3 exposure in the previously described NIOSH grain-elevator study.

Based upon these findings, when possible, the occupational bystander replicates from the registrant and NIOSH studies were consolidated into two categories: data for occupational bystanders working at or above the bin-top location vs. data for those working below this location. The areas of the studies at or above the bin-tops were the scale floor, and the gallery, bin floor, or distributor floor. The area below the bin-top location sampled in the studies is the basement, also known as the “tunnels”. In addition to these two categories, a third category was made for the occupational bystander that worked both within and outside of the grain-elevator during the work-shift. For samples taken during application and the subsequent fumigation, the numbers of replicates for the bystander on or above the floor of the grain-elevator containing the bin-top openings are 10 for the registrant study and 9 for the NIOSH study. The numbers of replicates for occupational bystanders working below the bin-tops are 3 for the registrant study and 3 for the NIOSH study. Finally, the numbers of replicates for the occupational bystander that worked both inside and outside of the grain-elevator are 6 for the registrant study and 3 for the NIOSH study. The mean sampling periods for the bystanders at or above the floor containing the bin-top openings are 3 hours for the registrant study and 6 hours for the NIOSH study. For the bystander located below this floor, the mean sampling times are 4 and 6 hours for the registrant and NIOSH studies, respectively. Finally, for the occupational bystander that worked both inside and outside of the grain-elevator, the mean sampling periods are 3 and 8 hours for the registrant and NIOSH studies, respectively. The seasonal exposure estimates were derived from the mean of the air concentration data which were corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study. The overall (registrant and NIOSH study data) mean breathing-zone PH_3 air concentration for the occupational bystander that worked at or above the bin-top level is 0.2 ppm. The corresponding mean for the occupational bystander that worked below the bin-top location is 0.1 ppm while that for the bystander that worked both inside and outside of the grain-elevator is 0.2 ppm. The short-term exposure estimates were derived from measured air concentrations which were corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate of the exposure study. The highest value of these adjusted data was used to estimate short-term exposure. The peak air concentration for the occupational bystander who worked at or above the bin-top level is 1.5 ppm. The corresponding highest values for the bystanders that worked below the bin-top level, and the bystanders that worked both inside and outside of the grain-elevator are 0.43 and 2 ppm, respectively (Table 9)

Table 9. Summary of Breathing-Zone PH_3 Air Concentration Data for Occupational Bystanders Working in Grain Elevators during Fumigant Application and Commodity Fumigation in Concrete Upright Bins

<table>
<tr><th>Data Source [a]</th><th>Location of Occupational Bystander [b]</th><th>Number of Replicates [c]</th><th>Mean Sampling Period (hr) [d]</th><th>Overall Mean PH_3 Air Concentration (ppm) [e]</th><th>Highest Replicate Air Concentration (ppm) [f]</th></tr>
<tr><td>Registrant</td><td>at or above bin-top level</td><td>10</td><td>3</td><td rowspan="6">bin-top
0.2

below bin-top
0.1

i/o elevator
0.2</td><td rowspan="6">bin-top
1.5

below bin-top
0.43

i/o elevator
2</td></tr>
<tr><td>Registrant</td><td>below bin-top level</td><td>3</td><td>4</td></tr>
<tr><td>Registrant</td><td>inside and outside of grain-elevator</td><td>6</td><td>3</td></tr>
<tr><td>NIOSH</td><td>at or above bin-top level</td><td>9</td><td>6</td></tr>
<tr><td>NIOSH</td><td>below bin-top level</td><td>3</td><td>6</td></tr>
<tr><td>NIOSH</td><td>inside and outside of grain-elevator</td><td>3</td><td>8</td></tr>
</table>

[a] Registrant: studies conducted on PH_3 exposure to occupational bystanders in grain elevators during application of aluminum phosphide fumigant via the auto-dispenser or manual application methods (occupational bystander exposure data for two application methods was combined) [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. NIOSH: studies conducted by the National Institutes of Occupational Safety and Health on PH_3 exposure to occupational bystanders in grain elevators during application of aluminum phosphide fumigant via the auto-dispenser or manual application methods (occupational bystander exposure data for the two application methods was combined) (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987).

[b] Occupational bystanders sampled in the studies were located in work areas at or above the level of the bin-top opening (i.e., bin floor/distributor floor/gallery or scale floor), in work areas below the bin-top opening (i.e., basement/tunnels), or both inside and outside of the grain-elevator.

[c] A replicate represents the work-shift (12 and 9.7 hrs TWA for short-term and intermediate-term exposure estimates, respectively) breathing-zone PH_3 air concentration for one worker. If more than one sample was taken for the worker during the workshift, the mean of the samples was used to represent the work shift breathing-zone air concentration.

[d] Mean amount of time that air in breathing-zone of occupational bystander was sampled for PH_3. The mean number of hours for the application period is 9.7. The sampling period air concentration, although shorter than the 9.7- or 12-hr work-shift period, is assumed to represent the PH_3 air concentration for the entire work-shift.

[e] The overall mean air concentration of replicate data (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), generated in the studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), work areas located below the bin openings (below bin-top), and inside and outside of the grain-elevator (i/o elevator).

[f] The measured air concentrations were corrected for recovery if the mean recovery of the study was < 90%. The air concentrations were then multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. Replicates were generated in the studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), work areas located below the bin openings (below bin-top), and inside and outside of the grain-elevator (i/o elevator). The highest values were used to estimate short-term exposure. The data set for the occupational bystander located at or above the bin-top location consists of 20 replicates with breathing-zone air concentrations ranging from 0.03 to 1.5 ppm. The data set for the occupational bystander located below the bin-top location consists of 6 replicates ranging in value from 0.004 to 0.43 ppm. The data set for the occupational bystander located inside and outside of the grain-elevator during the work shift consists of 9 replicates ranging in value from 0.01 to 2 ppm.

The occupational bystander scenario with the highest exposure value was used to estimate occupational bystander exposure during fumigant application and commodity fumigation. Hence, the bystander which worked both inside and outside of the grain-elevator with a peak breathing-zone air concentration of 2 ppm and a mean phosphine air concentration of 0.2 ppm was used to estimate exposure.

For samples taken post-application but during the subsequent fumigation, the occupational bystanders were located at or above the bin-top level, below the bin-top level, and inside/outside of the grain-elevator. For the samples taken from occupational bystanders located at or above the bin-top level of the grain-elevator, 2 replicates were generated in the registrant study and one in the NIOSH study. For the occupational bystander located below the bin-top level, 2 replicates were generated in the registrant study for the worker located in the tunnels of the grain-elevator. Finally, for the occupational bystander working both inside and outside of the grain-elevator, 14 replicates were generated in the registrant study. The mean sampling periods for the occupational bystander located at or above the bin-top level, below the bin-top level, and inside/outside of the grain-elevator during the work shift are 4.3, 3.3, and 3 hours, respectively. The overall (registrant and NIOSH study data) mean breathing-zone PH_3 air concentration (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), for the occupational bystander that worked at or above the bin-top level is 0.2 ppm. The corresponding mean for the occupational bystander that worked below the bin-top location is 0.09 ppm while that for the bystander that worked both inside and outside of the grain-elevator is 0.14 ppm. The highest value of the combined data (corrected for recovery if < 90%, multiplied by the maximum product label application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), for the occupational bystander who worked at or above the bin-top level is 0.96 ppm. The corresponding highest values for the bystanders that worked below the bin-top level and the bystanders that worked both inside and outside of the grain-elevator are 0.22 and 0.99 ppm, respectively (Table 10).

Table 10. Summary of Breathing-Zone Phosphine Air Concentration Data for Occupational Bystanders Working in Grain Elevators Post-Application but during Commodity Fumigation in Concrete Upright Bins

<table>
<tr><th>Data Source [a]</th><th>Location of Occupational Bystander [b]</th><th>Number of Replicates [c]</th><th>Mean Sampling Period (hr) [d]</th><th>Overall Mean PH_3 Air Concentration (ppm) [e]</th><th>Highest Replicate Air Concentration (ppm) [f]</th></tr>
<tr><td>Registrant</td><td>at or above bin-top level</td><td>2</td><td>3.4</td><td rowspan="4">bin-top
0.2

below bin-top
0.09

i/o elevator
0.14</td><td rowspan="4">bin-top
0.96

below bin-top
0.22

i/o elevator
0.99</td></tr>
<tr><td>Registrant</td><td>below bin-top level</td><td>2</td><td>3.3</td></tr>
<tr><td>Registrant</td><td>inside and outside of grain-elevator</td><td>14</td><td>3</td></tr>
<tr><td>NIOSH</td><td>at or above bin-top level</td><td>1</td><td>6</td></tr>
</table>

[a] Registrant: studies conducted on PH_3 exposure to applicators and occupational bystanders in grain elevators. [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. NIOSH: studies conducted by the National Institutes of Occupational Safety and Health on PH_3 exposure to applicators and occupational bystanders in grain elevators (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987).

[b] Occupational bystanders sampled in the studies were located in work areas at or above the level of the bin-top opening (i.e., bin floor/distributor floor/gallery or scale floor), in work areas below the bin-top opening (i.e. basement/tunnels), or both inside and outside of the grain-elevator.

[c] A replicate represents the work-shift (12 and 9.7 hrs TWA for short-term and intermediate-term exposure estimates, respectively) breathing-zone PH_3 air concentration for one worker. If more than one sample was taken for the worker during the work shift, the mean of the samples was used to represent the work shift breathing-zone air concentration.

[d] Mean amount of time that air in breathing-zone of occupational bystander was sampled for PH_3. The mean number of hours for the application period is 9.7. The sampling period air concentration, although shorter than the 9.7- or 12-hr work-shift period, is assumed to represent the PH_3 air concentration for the entire work-shift.

[e] The overall mean air concentration of replicate data (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), generated in the registrant and NIOSH studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), work areas located below the bin openings (below bin-top), and inside and outside of the grain-elevator (i/o elevator).

[f] The measured air concentrations were corrected for recovery if the mean recovery of the study was < 90%. The air concentrations were then multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. Replicates were generated in the studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), work areas located below the bin openings (below bin-top), and inside and outside of the grain-elevator (i/o elevator). The highest values were used to estimate short-term exposure. The data set for the occupational bystander located at or above bin-top level consists of 3 replicates with breathing-zone air concentrations ranging in value from 0.16 to 0.96 ppm. The data set for the occupational bystander located below the bin-top level consists of 2 replicates both equal to 0.22 ppm. The data set for the occupational bystander located inside and outside of the grain-elevator during the work shift consists of 14 replicates ranging in value from 0.005 to 0.99 ppm.

The occupational bystander scenario with the highest short-term breathing-zone air concentration was used to estimate occupational bystander exposure post-application and during fumigation. Hence, the bystander which worked both inside and outside of the grain-elevator with a peak breathing-zone air concentration of 0.99 ppm and a mean phosphine air concentration of 0.14 ppm was used to estimate exposure.

In addition to breathing-zone samples taken during application and fumigation, and post-application and fumigation, samples were taken from occupational bystanders after the grain had been aerated. These data were generated in the registrant study. The bulk of these samples were taken from workers located outside of the grain-elevator. These individuals worked in the office, carried out maintenance, loaded rail cars, and unloaded trucks. Six replicates were generated with mean sampling time of 2.6 hours. The mean of the measured air concentrations taken from these workers located outside of the grain-elevator is 0.07 ppm. Prior to calculating the mean, the breathing-zone phosphine air concentrations were corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study. The highest replicate air concentration of the data, following correction for recovery if < 90%, multiplication by the maximum product label application rate, and division by the application rate used in the exposure study, is 0.51 ppm. In addition to workers located outside of the grain-elevator, one worker spent the work shift both inside and outside of the grain-elevator. The sampling time for this worker was 2.6 hours and the breathing-zone air concentration, following correction for recovery if < 90%, multiplication by the maximum product label application rate, and division by the application rate used in the exposure study was 0.14 ppm. Two replicates were generated for an occupational bystander which, worked in the scale room located above the bin-top level in the grain-elevator. The mean sampling time for this type of worker is 2.7 hours. The mean of the measured air concentrations taken from these workers is 0.09 ppm. Prior to calculating the mean, the breathing-zone phosphine air concentrations were corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study. The highest replicate air concentration of the data, following correction for recovery if < 90%, multiplication by the maximum product label application rate, and division by the application rate used in the exposure study, is 0.23 ppm. One replicate was generated for a worker in the tunnels located below the bin-top level of the grain-elevator. The sampling time was 3.2 hours and the breathing-zone air concentration was 0.14 ppm (Table 11).

Table 11. Summary of Breathing-Zone Phosphine Air Concentration Data for Occupational Bystanders Working Inside and/or Outside of Grain Elevators after Aeration of Grain in Concrete Upright Bins

<table>
<tr><th>Data Source [a]</th><th>Location of Occupational Bystander [b]</th><th>Number of Replicates [c]</th><th>Sampling Period (hr) [d]</th><th>Overall Mean PH_3 Air Concentration (ppm) [e]</th><th>Short-Term Exposure Air Concentration (ppm) [f]</th></tr>
<tr><td>Registrant</td><td>at or above bin-top level</td><td>2</td><td>2.7*</td><td rowspan="4">bin-top
0.09

outside of elevator
0.07</td><td rowspan="4">bin-top
0.23

below bin-top
0.14

outside of elevator
0.51

i/o elevator
0.14</td></tr>
<tr><td>Registrant</td><td>below bin-top level</td><td>1</td><td>3.2</td></tr>
<tr><td>Registrant</td><td>outside of the grain-elevator</td><td>6</td><td>2.6*</td></tr>
<tr><td>Registrant</td><td>inside and outside of grain-elevator</td><td>1</td><td>2.6</td></tr>
</table>

[a] Registrant: studies conducted on PH_3 exposure to applicators and occupational bystanders in grain elevators. [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

[b] Occupational bystanders sampled in the studies were located in work areas at or above the level of the bin-top opening (i.e. bin floor/distributor floor/gallery or scale floor), in work areas below the bin-top opening (i.e. basement/tunnels), or both inside and outside of the grain-elevator.

[c] A replicate represents the work-shift (12 and 9.7 hrs TWA for short-term and long-term exposure estimates, respectively) breathing-zone PH_3 air concentration for one worker. If more than one sample was taken for the worker during the work shift, the mean of the samples was used to represent the work shift breathing-zone air concentration.

[d] Mean amount of time that air in breathing-zone of occupational bystander was sampled for PH_3. The mean number of hours for the application period is 9.7. The sampling period air concentration, although shorter than the 9.7- or 12-hr work-shift period, is assumed to represent the PH_3 air concentration for the entire work-shift.

[e] The overall mean air concentration of replicate data (corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application rate used in the exposure study), generated in the studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), and outside of the elevator. The data set for the occupational bystander located at or above bin-top level consists of 2 replicates with breathing-zone air concentrations ranging in value from 0.08 to 0.1 ppm. The data set for the occupational bystander located below the bin-top level consists of 1 replicate equal to 0.06 ppm. The data set for the occupational bystander located inside and outside of the grain-elevator during the work shift consists of 1 replicate equal to 0.06. The data set for the occupational bystander working outside of the grain-elevator throughout the entire work shift consists of 6 replicates ranging in value from 0.02 to 0.21 ppm.

[f] The short-term exposure air concentrations consisted of the highest or, in the case of one replicate value, only air concentration. The replicate air concentrations were corrected for recovery if <90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. Replicates were generated in the studies shown for the occupational bystander working at or above the openings at the top of the bins (bin-top), work areas located below the bin openings such as the tunnels (below bin-top), outside of the grain-elevator, and inside and outside of the grain-elevator (i/o elevator). The occupational bystander scenario with the highest breathing-zone air concentration (i.e., the worker located outside of the grain-elevator) was used to estimate short-term exposure for all of the other post-aeration occupational bystander scenarios.

*Value shown is mean of replicate sampling times

The occupational bystander scenario with the highest exposure value was used to estimate occupational bystander exposure post-aeration of the fumigated commodity. Hence, the bystander which worked outside of the grain-elevator with a peak breathing-zone air concentration of 0.51 ppm and a mean phosphine air concentration of 0.07 ppm was used to estimate exposure.

<u>Estimation of Work-Shift Period for the Applicator and Occupational Bystander</u>

The arithmetic mean of work-shift periods of the applicators and occupational bystanders in both the registrant and NIOSH studies is 9.7 hours. The work-shift periods listed in the seven studies range from 8 to 12 hours. In some of the registrant studies, a range of 8 to 10 hours was given for the length of the work-shift. In these cases, to be health-protective, the higher number (i.e. 10 hours) was used to calculate the mean. The mean sampling periods of the studies for both the applicators and occupational bystanders ranged from 2.6 to 8 hours which is less than the mean work-shift period of 9.7 hours. However, for exposure assessment purposes, the TWA PH_3 air concentrations measured over these sampling periods were assumed to exist for the entire work period. For estimating short-term exposure, the longest reported work-shift period (i.e. 12 hours) was used. For intermediate-term exposure, the mean value of 9.7 hours was used for estimating exposure.

Applicator (Auto-dispenser)

<u>Short-Term Exposure Estimate</u>

In the absence of PPE, the applicator operating the auto-dispenser is anticipated to being exposed to a PH_3 air concentration of 5.8 ppm (12 hr TWA) each workday for up to one week. However, as mentioned earlier, according to the product labels, a handler must use respiratory protection for phosphine air concentrations above the 8-hr TWA PEL of 0.3 ppm. A NIOSH/MSHA approved full-face gas mask-phosphine canister combination may be used for phosphine air concentrations up to 15 ppm. The protection factor used by DPR for this type of PPE is 98% (Beauvais, 2011). Hence, the estimated phosphine air concentration of 5.8 ppm to which the applicator would be exposed to for 12 hr TWA, would be reduced to 0.12 ppm (Table 12).

Table 12. Exposure Estimates for the Applicator Operating the Auto-Dispenser or Manually Adding Aluminum Phosphide to Commodity in the Concrete Upright Bins of Grain-Elevators [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator (auto-dispenser) [e]	0.12	0.02	0.01
applicator (manual) [f]	0.01	0.07	0.05

[a] Exposure estimates generated in this table are from breathing-zone air concentrations which have been corrected for recovery if <90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. The data from both the registrant [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015] and NIOSH (NIOSH Composite Report, 1987, NIOSH Report 149.10, 1986, NIOSH Report 149.12, 1986, and NIOSH Report 149.18, 1987) studies were consolidated and used to estimate exposures. Studies are summarized in Table 8. The exposure estimates, were adjusted for the use of respiratory protection. The air concentrations estimated required the use of a respiratory protection such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination. DPR uses a protection factor of 98% for this type of PPE.

[b] Short-Term Exposure: phosphine air concentration to which applicator is exposed to for 12 hr TWA/day for up to one week. Short-term exposures were calculated from the highest measured phosphine air concentrations which were corrected for recovery, if <90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study.

[c] Seasonal Exposure: phosphine air concentration to which applicator is exposed to for 9.7 hr TWA/day for a season of 8 months. Seasonal exposure was made equal to the mean of the measured air concentrations which were corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide (i.e., 0.06 grams/ft^3), and divided by the application rate used in the exposure study.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The short-term exposure for the applicator using the auto-dispenser was initially made equal to 5.8 ppm, the highest TWA breathing-zone air concentration generated for this scenario. This value was the highest work shift breathing-zone air concentration of 15 replicates, ranging from 0.2 to 5.8 ppm. The exposure estimate, adjusted for the use of a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination, was reduced from 5.8 to 0.12 ppm.

[f] The manual applicator was located below the bin-top level of the grain-elevator. The data set for this scenario consisted of 4 replicates. The replicate phosphine breathing-zone air concentrations ranged in value from 0.01 to 0.6 ppm. The highest value was used to estimate short-term exposure. With the use of a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination, this value is reduced from 0.6 to 0.01 ppm. Seasonal and annual exposure estimates were generated using the mean of the 4 replicates or 0.07 ppm.

Seasonal Exposure Estimate

As mentioned in the PUR section, the estimated seasonal use of aluminum phosphide for fumigation of dry flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. Since these goods would be stored and fumigated in the concrete upright bins of the grain-elevator, this season was used to estimate seasonal exposure to the workers in this structure. Hence, without a respirator, the applicator is anticipated to be exposed to a PH_3 air concentration of 0.8 ppm (9.7 hr TWA) each day for 8 months of the year. Since the concentration is above the 0.3 ppm PEL, respiratory protection such as a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination would be required. This PPE with the 98% protection factor would reduce the 0.8 ppm concentration to 0.02 ppm (Table 12).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator, without a respirator, is anticipated to be exposed to 0.5 ppm PH_3 (9.7 hr TWA) each day over the course of the year. Since the concentration is above the 0.3 ppm PEL, respiratory protection such as a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination would be required. This PPE with the 98% protection factor would reduce the 0.5 ppm concentration to 0.01 ppm. (Table 12).

Applicator (Manual Application)

Short-Term Exposure Estimate

In the absence of PPE, the applicator conducting manual application of the fumigant is anticipated to being exposed to a PH_3 air concentration of 0.6 ppm (12 hr TWA) each workday for up to one week (Table 12). However, this air concentration being above the 0.3 ppm PEL, would require the use of respiratory protection such as a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination, which would reduce the breathing-zone air concentration to 0.01 ppm.

Seasonal Exposure Estimate

As mentioned in the PUR section, the estimate seasonal use of aluminum phosphide for fumigation of dry-flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. Since these goods would be stored and fumigated in the concrete upright bins of the grain-elevator, this season was used to estimate seasonal exposure to the workers in this structure. Hence, the applicator is anticipated to be exposed to a PH_3 air concentration of 0.07 ppm (9.7 hr TWA) each day for 8 months of the year (Table 12).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.05 ppm PH_3 (9.7 hr TWA) each day over the course of the year (Table 12).

Occupational Bystander

Exposure during Fumigant Application and Commodity Fumigation

Short-Term Exposure Estimate

Of all the occupational bystanders associated with commodity fumigation in grain-elevators, the bystander working both inside and outside of the grain-elevator had the highest potential exposure level (i.e., 2 ppm). This particular scenario was used to represent occupational bystander exposure during fumigation application and commodity fumigation. Since this air concentration exceeds the 0.3 ppm 8-hr TWA PEL, the worker would be required to use a respirator such as the NIOSH/MSHA approved full-face gas mask-phosphine canister combination. The protection factor for this PPE is 98%. Hence, the 2 ppm short-term exposure air concentration would be reduced to 0.04 ppm (Table 13).

Table 13. Occupational and Residential Bystander Exposure to Phosphine during Fumigant Application and Fumigation, Fumigation (Post-Application), and Post-Aeration of Commodity in the Concrete Upright Bins of Grain-Elevators [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
Fumigant Application and Commodity Fumigation			
occupational bystander (inside and outside of grain-elevator) [e]	0.04	0.2	0.13
residential bystander [f]	0.1	0.1	0.07
Commodity Fumigation (Post-Application)			
occupational bystander (inside and outside of grain-elevator) [g]	0.02	0.14	0.09
residential bystander [f]	0.1	0.1	0.07
Post-Aeration			
occupational bystander (outside of grain-elevator) [h]	0.01	0.07	0.05
residential bystander [f]	0.1	0.1	0.07

[a] The data from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015] were used to estimate exposures. Studies are summarized in Tables 9 – 11.

[b] Short-Term Exposure (occupational bystander): phosphine air concentration to which the occupational bystander is exposed to for 12 hours TWA/day, for up to one week. Except for the residential bystander, short-term exposure was calculated from the highest measured phosphine air concentrations. These air concentrations were corrected for recovery if <90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study. If an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator and 99.99% for SCBA). Short-Term Exposure (residential bystander): phosphine air concentration to which the residential bystander is exposed to for 24 hours TWA/days, for up to one week. Due to a lack of data, short-term exposure was assumed to be the 24-hr equivalent of the 8-hr TWA PEL of 0.3 ppm (i.e., 0.1 ppm). The residential bystander was assumed to not be wearing respiratory protection.

[c] Seasonal Exposure (occupational bystander): phosphine air concentration to which the occupational bystander is exposed to for 9.7 hr TWA/day for a season of 8 months. Except for the residential bystander, seasonal exposure was made equal to the mean of the measured air concentrations which were corrected for recovery if the mean recovery of the study was < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide (i.e., 0.06 grams/ft^3), and divided by the application rate used in the exposure study. If an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator with canister and 99.99% for SCBA). Seasonal Exposure (residential bystander): the short-term exposure air concentration of 0.1 ppm (24 hr TWA) was used as the seasonal exposure air concentration. The season was estimated to be 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The data set for the occupational bystander located inside and outside of the grain-elevator during the work shift and during fumigant application and commodity fumigation consists of 9 replicates ranging in value from 0.01 to 2 ppm.

[f] There were no TWA breathing-zone phosphine air concentration data for the residential bystander. Hence, the 24-hr TWA equivalent of the 0.3 ppm 8-hr TWA PEL (i.e., 0.1 ppm) was used for short-term exposure. Seasonal and annual exposures were derived from this value. The residential bystander was assumed to not use respiratory protection.

[g] The data set for the occupational bystander located inside and outside of the grain-elevator during the work shift post-application consists of 14 replicates ranging from 0.005 to 0.99 ppm.

[h] The data set for the occupational bystander working outside of the grain-elevator throughout the entire work shift after aeration of the commodity consists of 6 replicates ranging in value from 0.05 to 0.51 ppm.

Seasonal Exposure Estimate

As mentioned in the PUR section, the estimated seasonal use of aluminum phosphide for fumigation of dry flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. Since these goods would be stored and fumigated in the concrete upright bins of the grain-elevator, this season was used to estimate seasonal exposure to the workers in this structure. Hence, the occupational bystander working both inside and outside of the grain-elevator is anticipated to be exposed to a phosphine air concentration of 0.2 ppm for 9.7 hr TWA per day for 8 months/year (Table 13).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the occupational bystander that works both inside and outside of the grain-elevator is anticipated to be exposed to a daily (9.7 hr TWA) phosphine air concentration of 0.13 ppm (Table 13).

Exposure Post-Application and during Commodity Fumigation

Short-Term Exposure Estimate

Of all the occupational bystander scenarios for exposure post-application and during commodity fumigation, the bystander working both inside and outside of the grain-elevator had the highest potential exposure level (i.e., 0.99 ppm). This particular scenario was used to represent occupational bystander exposure post-application and during commodity fumigation. Since this air concentration exceeds the 0.3 ppm 8-hr TWA PEL, the worker would be required to use respiratory protection such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination. The protection factor for this PPE is 98%. Hence, the 0.99 ppm short-term exposure air concentration would be reduced to 0.02 ppm (Table 13).

Seasonal Exposure Estimate

As mentioned in the PUR section, the estimated seasonal use of aluminum phosphide for fumigation of dry flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. Since these goods would be stored and fumigated in the concrete upright bins of the grain-elevator, this season was used to estimate seasonal exposure to the workers in this structure. Hence, the occupational bystander working both inside and outside of the grain-elevator is anticipated to be exposed to a phosphine air concentration of 0.14 ppm for 9.7 hr TWA per day for 8 months/year (Table 13).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the occupational bystander that works both inside and outside of the grain-elevator is anticipated to be exposed to a daily (9.7 hr TWA) phosphine air concentration of 0.09 ppm (Table 13).

Exposure Post-Aeration of Fumigated Commodity

Short-Term Exposure Estimate

Of all the occupational bystander scenarios for exposure post-aeration of fumigated commodity, the bystander working outside of the grain-elevator had the highest potential exposure level (i.e., 0.51 ppm). This particular scenario was used to represent occupational bystander exposure post-aeration. Since this air concentration exceeds the

0.3 ppm 8-hr TWA PEL, the worker would be required to use respiratory protection such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination. The protection factor for this PPE is 98%. Hence, the 0.51 ppm short-term exposure air concentration would be reduced to 0.01 ppm (Table 13).

Seasonal Exposure Estimate

As mentioned in the PUR section, the estimated seasonal use of aluminum phosphide for fumigation of dry flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. The occupational bystander working just outside of the grain-elevator is anticipated to be exposed to a phosphine air concentration of 0.07 ppm for 9.7 hr TWA per day for 8 months/year (Table 13).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the occupational bystander that works both inside and outside of the grain-elevator is anticipated to be exposed to a daily (9.7 hr TWA) phosphine air concentration of 0.05 ppm (Table 13).

Residential Bystander

Due to a lack of useable data, the residential bystander near a grain-elevator was assumed to be exposed to a PH_3 air concentration of 0.1 ppm (24 hr TWA) which is equivalent to the 8-hr PEL of 0.3 ppm as stated on the product labels. In separate studies, the registrants and the California Air Resources Board (CARB) measured the PH_3 air concentrations outside of structures, other than grain-elevators, which were undergoing fumigation or aeration. However, the data was not used as surrogate data for the grain-elevator because of the lack of similarity. The structures monitored in the registrant study were bins, containers, tarped structures, trailers, warehouses, a fumigation chamber, a "hut", silos, and grain storage tanks [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022]. The CARB staff measured phosphine air concentrations outside of a fumigation chamber (CARB, 2008). All of these structures are much simpler in design than the grain-elevator which contains not only concrete upright bins, but a headhouse with conveyor systems, a basement or tunnels area, and docks for shipping/receiving grain.

Although the data for these structures was unsuitable as surrogate data for the grain-elevator, data from the registrant and CARB studies suggest that PH_3 air concentrations outside of these storage structures could reach levels above the product label PEL restriction of 0.3 ppm (8-hr TWA). For example, in the registrant study, during the aeration step, the mean of the PH_3 air concentrations, measured using colorimetric detector tubes, from 0 to 3 feet outside of six different warehouses was 3 ppm. The application rates for the magnesium phosphide used to fumigate the commodity in the warehouses ranged from 0.03 to 0.044 grams of phosphine/cubic foot. After multiplying the air concentrations with the maximum product label application rate of 0.145 grams of phosphine/cubic foot, and then dividing these values by the exposure study application rate, the mean of the air concentrations increases to 12.8 ppm. Moreover, the corresponding value for a large grain storage structure called a "hut" during fumigation is 5.8 ppm [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022].

In the CARB study, the researchers obtained 4-hr TWA air concentrations at locations ranging from 15 to 25 feet from the outside of a fumigation chamber during fumigation. The samples were obtained using sampling pumps which pressurized six (6)-liter “Silco” canisters with ambient air. Each canister was made of metal and had a plastic lining to prevent loss of the analyte. The air samples were obtained from a height of 1.5 meters above ground level. The sampling flow-rate was 45 ml/min and three (4)-hour samples were obtained over the fumigation period. The estimated limit of quantitation for the analytical method was 0.002 ppm. The commodity in the chamber was fumigated using aluminum phosphide pellets applied at a rate of 0.02 grams of PH_3/cubic foot. This application rate yielded a peak 4-hr TWA PH_3 sample air concentration of 58.33 µg/m^3 or 0.04 ppm. However, if multiplied by the product label maximum application rate of 0.145 grams of PH_3/cubic foot, and then divided by the application rate used in the exposure study, the air concentration becomes 0.3 ppm.

Two field fortification samples were conducted to measure the recovery of the analyte after being stored in the Silco container throughout the entire monitoring period. One of the samples had a relatively low recovery (i.e., 17.2%). This was thought to be potentially due to the plastic liner of the container. The authors stated that the canisters had been used in various monitoring studies for 10 years, and as a result, the plastic liners of some containers may have degraded, allowing the PH_3 to contact and react with the metal container. Hence, the recoveries from one or more of the sample canisters may have been reduced, resulting in sample loss. As a result, the aforementioned highest measured 4-hr TWA air concentration of 0.04 ppm may have been less than the actual phosphine air concentration (CARB, 2008).

Bystander exposures above the PEL of 0.3 ppm 8-hr TWA seem especially plausible since no buffer-zones are required to exist between the grain-elevator and a residence. However, as stated on the product labels, the applicator must prevent exposure above the PEL and STEL to the residential bystander. Due to the possibility of exposure, the product label exposure restrictions (i.e. PEL and STEL), and the need to be health-protective, the residential bystander is anticipated to be exposed to the PEL of 0.3 ppm (8 hr TWA). Since the bystander is assumed to reside adjacent to the grain-elevator, the 24-hr equivalent of the 8 hr TWA of 0.3 ppm which is 0.1 ppm (24 hr TWA) was used as the short-term exposure estimate (Table 13).

<u>Seasonal Exposure Estimate</u>

As mentioned in the PUR section, the estimated seasonal use of aluminum phosphide for fumigation of dry flowable commodities (i.e. nuts and grains) and space fumigation for the years of 2006-10 is 8 months. The residential bystander is anticipated to be exposed to the short-term air concentration of 0.1 ppm (24 hr TWA) for 8 months annually (Table 13).

<u>Annual Exposure Estimate</u>

Amortizing the seasonal exposure over the entire year, the residential bystander is anticipated to be exposed to 0.07 ppm PH_3 (24 hr TWA) throughout the year (Table 13).

Commodity Fumigation in the Farm Bin

Applicator

The data used to estimate exposure was obtained from the aforementioned registrant task force study. In the study, the farm bins were described as being grain-storage bins which were cylindrical with conical roofs, being constructed of corrugated metal, and as having volumes of less than 62,000 cubic feet. The mean volume of the farm bins in the registrant study is 19,304 cubic feet. In one case, the bins were described as being open grain boxes located within a grain-elevator [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The exposure estimates generated in this section are for handlers, occupational bystanders, and residential bystanders potentially exposed to phosphine during fumigation and aeration of grain within the farm bin.

Treatment of the grain within the farm bin consists of fumigation followed by aeration. However, in the registrant study, only fumigation of the grain was monitored. The registrant collected breathing-zone samples from workers conducting 24 commodity fumigations in a total of 24 farm bins. Twenty-one of the commodity fumigations were conducted using aluminum phosphide tablet or pellet formulations while 3 of the fumigations were carried out using aluminum phosphide containing bag belts. The measured air concentrations were corrected for recovery, if less than 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. In the farm bins studies utilizing bag belts, the registrant states that "the bag belts release phosphine more slowly than most other product forms" [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. However, one of the highest phosphine breathing-zone air concentrations measured was for a worker applying bag belts. The mean of the 3 bag belt replicates which were corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and then divided by the application rate used in the exposure study, is 0.6 ppm. This air concentration is nearly the same as the corresponding mean for the entire study (i.e., 0.7 ppm). Hence, the three replicates for bag belts were incorporated with the other replicates for estimating exposure. In total, 16 replicates were generated for the worker applying or assisting with application of the fumigant. A replicate consisted of the work shift breathing-zone air concentration for one worker. This work shift breathing-zone air concentration may consist of one sample or the mean of multiple samples taken from the worker during the work shift. According to this definition, 3 replicates were generated for the occupational bystander who monitored the phosphine air concentrations near the applicator during application of fumigant.

According to the product labels, in addition to aluminum phosphide tablets, pellets, and bags, the grain within the farm bin can also be treated with bags containing magnesium phosphide, blister packs or polymeric fleece containing aluminum phosphide or magnesium phosphide, polyethylene strips or plates impregnated with magnesium phosphide, or, via a phosphine generator, granules containing aluminum phosphide or magnesium phosphide. Farm bins can also be fumigated using cylinderized phosphine gas. Due to a lack of data, the estimates generated for the farm bin using tablets, pellets, and bag belts act as surrogate estimates for these other formulations. In addition, some of the product labels have the term “grain storage tank” listed as a treatment site. Due to a lack of data, the estimates generated for the farm bin were used as surrogate estimates for this structure.

The fumigation procedure consisted of 3 basic steps: preparation of the structure for fumigation, entering the structure to apply the fumigant, and then exiting the structure. In the study, prior to fumigation, vents, and hatches in the farm bin were sealed. The applicator then opened one of the seals and entered the facility to apply the fumigant via one of four different methods. These methods consist of the “walk-in” method, the “RPC method”, the “probe method”, and the “subsurface hand method”. The walk-in method consists of the applicator walking through the grain and shaking fumigant from a flask held several feet above the surface. With the second method, called the RPC method, the applicator submerges a flask 2 to 4 inches below the surface of the grain and then shakes out the fumigant as the flask is lifted back out. The probe method consists of applying the fumigant through a pipe with one end inserted a foot or more below the surface of the grain. The pellets or tablets are deposited into the grain as the pipe was withdrawn. The fourth technique or subsurface hand method consists of the applicator working a handful of fumigant approximately 12 inches below the surface of the grain. Following the application step, the handler, in cases where the structure was especially leaky, covered the grain with a tarpaulin. The worker then exited the bin, and sealed the exit [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The current product labels for tablet and pellet formulations, instruct the applicator to apply the fumigant using the probe method or via scattering the fumigant on the surface of the grain (i.e., walk-in method). According to the product labels fumigant containing bags can be applied to the grain via scattering over the surface, “stepped” or buried into the grain, or applied via the probe method.

The handler’s breathing-zone sampling period and the number of farm bins treated per day in the study were not utilized to estimate the duration of phosphine exposure per work day. The sampling period included the steps involved in the actual fumigation (i.e. opening of fumigant container and applying fumigant) and may have also included other activities such as preparing the structure for fumigation or covering the fumigated grain in tarpaulin. The greatest number of farm bins fumigated/day in the study is 5. The longest breathing-zone sampling period of the study for the applicators conducting commodity fumigation in the farm bins is 26 minutes. This sampling period included preparation of the bin for fumigation, opening the fumigant containers, entering the bin, applying the fumigant, exiting the bin, and taping the seal around the entry hatch. Hence, based on the study, the greatest potential exposure period/day for handlers fumigating farm bins is 5 x 26 minutes or 130 minutes. However, a greater number of structures could be fumigated. Hence, the default work period of 8 hours was used to estimate short-term exposure [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

The short-term phosphine exposures to the applicator conducting commodity fumigation in the farm bin were estimated using the highest work shift breathing-zone phosphine air concentration, corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. The mean of the work shift breathing-zone air concentrations, which were corrected for recovery if less than 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and subsequently divided by the application ate used in the exposure study, was used to estimate seasonal exposure. The work shift breathing-zone air concentration may consist of one sample or, if multiple samples were taken from the worker over the course of the work shift, the mean of these samples.

Short-Term Exposure Estimate

The highest measured air concentration was corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. The result (i.e., 4.8 ppm) is assumed to be the 8-hr TWA work shift breathing-zone air concentration. Since this estimate exceeds the 8-hr TWA PEL of 0.3 ppm, the worker is assumed to be wearing respiratory protection such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination. This respirator is assumed to reduce the 4.8 ppm phosphine breathing-zone air concentration to 0.1 ppm (Table 14).

Table 14. Exposure Estimates for the Applicator, Aerator, Occupational Bystander, and Residential Bystander during Commodity Fumigation and Aeration in the Farm Bin [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.1	0.007	0.005
aerator [f]	0.02	0.3	0.2
occupational bystander [g] (air monitor)	0.04	0.01	0.008
occupational bystander [h] (adjacent to farm bin during fumigation)	0.3	0.3	0.2
occupational bystander [h] (adjacent to farm bin during aeration)	0.3	0.3	0.2
residential bystander [i] (adjacent to farm bin during fumigation and aeration)	0.1	0.1	0.07

[a] Except for the occupational and residential bystanders adjacent to the farm bin during fumigation and aeration, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with canister and 99.99% for SCBA). Exposure estimates were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Due to a lack of data, the exposure estimates for the farm bin were chosen to act as surrogate exposure estimates for the applicator, aerator, occupational bystander, and residential bystander associated with fumigation and aeration of the grain storage tank which is listed on product labels. The estimates were also chosen to act as surrogates for the cylinderized phosphine gas and granular formulations which can also be used for commodity fumigation in the farm bin and grain storage tank.

[b] Short-Term Exposure: phosphine air concentration to which applicator, aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for up to one week

[c] Seasonal Exposure: phosphine air concentration to which applicator, aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] For the applicator exposure estimates generated in this EAD, the data set used to estimate short-term exposure for the applicator consists of 16 replicates ranging in value from 0.05 to 4.8 ppm.

[f] The data set used to estimate short-term exposure for the aerator is a surrogate data set from the warehouse study and consists of 10 replicates ranging in value from 0.16 to 1.2 ppm.

[g] Occupational bystander (air monitor): worker which measured phosphine air concentrations near applicator during application of fumigant. The data set used to generate the short-term exposure estimate for this scenario consists of 3 replicates ranging in value from 1.1 to 1.8 ppm.

[h] There are no TWA breathing-zone phosphine air concentration data for the occupational bystander adjacent to the farm bin during application/fumigation or aeration. Hence, the 8-hr TWA PEL value of 0.3 ppm was used to estimate the short- and long-term exposures.

[i] There are no TWA breathing-zone phosphine air concentration data for the residential bystander. Hence, the 24-hr TWA equivalent of the 0.3 ppm 8-hr TWA PEL (i.e., 0.1 ppm) was used for short-term exposure. The long-term exposures were also derived from this value.

Seasonal Exposure Estimate
The estimated fumigant use season for the farm bin is 8 months. The applicator with respiratory protection is anticipated to be exposed to a PH_3 air concentration of 0.007 ppm (8 hr TWA) each day for 8 months of the year (Table 14).

Annual Exposure Estimate
Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.005 ppm PH_3 (8-hr TWA) each day over the course of the year (Table 14).

Aerator

No aeration step was conducted in the registrant studies for farm bins. Therefore, the aerator exposure data of a registrant study on handler exposure in a fumigated cold weather tobacco warehouse was utilized as surrogate data. This structure is more similar to the farm bin than the other structures (i.e., box cars and bulk cars) for which aerator exposure data are available. The aeration was conducted four days after the fumigation which was conducted using polyethylene strips impregnated with magnesium phosphide. The first step in aeration consisted of opening the main doors to the warehouse and cutting the plastic barriers to the phosphine fumigant inside. This portion of the aeration had the highest measured phosphine air concentrations and greatest risk of exposure. The step took from sixty to ninety minutes to complete. Ten replicates were generated for the aerator in the warehouse study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest work shift breathing-zone air concentration, corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study, is 1.2 ppm. Assuming the aeration of farm bins takes the same amount of time/day as the fumigation, the estimated short-term exposure for the commercial applicator conducting aeration is 1.2 ppm for 130 minutes/day. However, a greater number of structures could be aerated. Hence, the default work period of 8 hours was used as the exposure duration. The mean of the work shift breathing zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate, and divided by the application rate used in the exposure study, is 0.3 ppm.

Short-Term Exposure Estimate
The handler wearing a full-face respirator supplied with a canister, with a 98% protection factor, and conducting aeration of the farm bin is anticipated to be exposed to a PH_3 air concentration of 0.02 ppm for 8 hours/day (Table 14).

Seasonal Exposure Estimate
The estimated fumigant use season for the farm bin is 8 months. The worker aerating farm bins is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 14).

Annual Exposure Estimate
Amortizing the seasonal exposure over the entire year, the aerator is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 14).

Occupational Bystander

For the farm bin, there are two potential occupational bystanders. The first was monitored for exposure in the registrant study for this structure and consists of a worker that assayed the atmosphere within the bin for unsafe phosphine levels during the application of fumigant. Three replicates were generated. The highest work shift breathing-zone air phosphine air concentration, corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study, is 1.8 ppm. The mean of the measured air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate, and divided by the application rate used in the exposure study, is 0.6 ppm. Assuming the monitor accompanied the applicator for each of the 5 fumigations, the short-term exposure estimate for this occupational bystander is ppm for 130 minutes/day. However, as mentioned earlier, a greater number of structures could be aerated. Hence, the default work period of 8 hours was used as the exposure duration.

<u>Short-Term Exposure Estimate</u>

The occupational bystander wearing respiratory protection such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination and monitoring phosphine air concentrations during application of fumigant is anticipated to be exposed to an 8 hr TWA PH_3 air concentration of 0.04 ppm (Table 14).

<u>Seasonal Exposure Estimate</u>

The estimated fumigant use season for the farm bin is 8 months. The occupational bystander or monitor accompanying the applicator and wearing respiratory protection such as a NIOSH/MSHA approved, full-face gas mask-phosphine canister combination is anticipated to be exposed to a PH_3 air concentration of 0.01 ppm (8 hr TWA) each day for 8 months of the year (Table 14).

<u>Annual Exposure Estimate</u>

Amortizing the seasonal exposure over the entire year, the occupational bystander is anticipated to be exposed to 0.008 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 14).

The second type of occupational bystander which could potentially be exposed to phosphine during the fumigation step is the bystander working outside of and adjacent to the farm bin. For this scenario, data from two separate studies were considered. These studies were the aforementioned registrant and CARB studies. In the registrant's investigation, the researchers monitored the phosphine air concentrations from 0 to 3 feet outside and downwind of the structure being fumigated and aerated. The type of monitoring device used in the study was a length-of-stain detector tube which provided instantaneous readings. The sampling was conducted at regular intervals following the initiation of the fumigation or aeration. For the application step, the monitoring time points were generally taken at the beginning of the application and then every 24 hours for up to 168 hours. In some cases the initial reading was taken 1, 12, 48, or 72 hours after the start of the application. The fumigation sites considered for this exposure scenario were treated with solid formulations containing aluminum phosphide or magnesium phosphide. Various structures for storing commodities were monitored including the "steel bin", "butler bin", "container", "warehouse", and "hut". These structures ranged in size from 1000 to 1,676,480 cubic feet. The highest phosphine air concentration measured outside of a structure undergoing commodity fumigation was 4 ppm. This air concentration was detected 0 to 3 feet downwind of the hut 24, 48, 72, and 96-hr after the start of the fumigation. For estimating short-term exposure, the air concentration was multiplied by the maximum product label application rate, and subsequently divided by the application rate used in the exposure study. Following these adjustments, the air concentration increased to 7.3 ppm. [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022].

The type of sampling utilized in this study could not be used to estimate exposure for the occupational bystander working outside of and adjacent to a structure undergoing commodity fumigation. As a worst-case scenario, the occupational bystander is assumed to work adjacent to the fumigated farm bin for 8 hr/day. However, the data collected does not provide a TWA value for the first 8 hours of fumigation which is the assumed time at which the occupational bystander may be working. Some of the sites monitored in the study such as the aforementioned hut, do show that the phosphine air concentrations could potentially exceed the 8-hr TWA PEL of 0.3 ppm stated on the product labels. Moreover, as described earlier, the peak measured 4-hr TWA PH_3 air concentration outside of the fumigation chamber in the CARB study, multiplied by the maximum product label application, and subsequently divided by the application rate used in the study was equal to or greater than 0.3 ppm (CARB, 2008). As a result, the assumed short-term exposure estimate for the occupational bystander working adjacent to a fumigated farm bin is the legal maximum allowable exposure of 0.3 ppm (8 hr TWA) as stated on the product labels. Any exposures beyond this level would require respiratory protection, which must reduce the 8-hr TWA exposure to 0.3 ppm or less.

<u>Short-Term Exposure Estimate</u>
The occupational bystander working adjacent to the farm bin during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each workday for up to one week (Table 14).

<u>Seasonal Exposure Estimate</u>
The estimated used season for the farm bin is 8 months. The occupational bystander working adjacent to the farm bin during fumigation or aeration is anticipated to be exposed to 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 14).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the occupational bystander is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 14).

In addition to the potential for exposure during fumigation is the risk of exposure during aeration of the structure. In the registrant study, the same structures mentioned earlier were also aerated following the fumigation. Air samples were taken from 0 to 3 feet downwind of each structure at the beginning of the aeration step and generally 1, 2, and 6 hours after the start of the aeration. In one case, the samples were taken at the beginning of the aeration and every 24 hours after that for up to 168 hours. Obtaining an 8-hr TWA exposure estimate for the occupational bystander was not possible using this data. However, in three of the structures monitored, at the start of the aeration and after 1 and 2 hours of aeration, the phosphine air concentrations ranged from 22 to 439 ppm. These data suggest that the air concentrations of phosphine may exceed the 0.3 ppm 8 hr TWA PEL stated on the product labels [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022].

For the aforementioned CARB study, unlike the fumigation stage, PEL level exposure is not suggested by the peak 4-hr TWA air concentration measured during the aeration phase of the study. After multiplying the air concentration by the maximum product label application rate, and subsequently dividing the result by the application rate used in the exposure study, the peak 4-hr TWA air concentration measured during aeration was 0.03 ppm. However, the aeration samples were taken at a relatively greater distance (i.e., 25 to 40 feet away from the fumigation chamber), and, as mentioned earlier, sample loss may have been an issue (CARB, 2008). As a result, the assumed short-term exposure estimate for the occupational bystander working adjacent to a fumigated farm bin undergoing aeration is the legal maximum allowable exposure of 0.3 ppm (8 hr TWA) as stated on the product labels.

<u>Short-Term Exposure Estimate</u>
The occupational bystander working adjacent to the farm bin during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each workday for up to one week (Table 14).

<u>Seasonal Exposure Estimate</u>
The estimated fumigant use season for the farm bin is 8 months. The occupational bystander working adjacent to the farm bin during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 14).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the occupational bystander is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 14).

Residential Bystander

The residential bystander is assumed to reside adjacent to the farm bin undergoing commodity fumigation or aeration. The data available to estimate potential phosphine exposure during fumigation and aeration are those described in the occupational bystander exposure section. Obtaining a 24-hr TWA exposure estimate from this data is not possible. Therefore, the highest legal maximum breathing-zone air concentration was used to estimate exposure. As mentioned earlier, this is the 8-hr TWA PEL of 0.3 ppm. Since the residential bystander is assumed to reside adjacent to the structure, the 24-hr

TWA equivalent of the PEL (i.e., 0.1 ppm) was used to estimate the short-term and long-term exposure estimates.

Short-Term Exposure Estimate
As stated earlier, the residential bystander is assumed to reside adjacent to the structure undergoing commodity fumigation or aeration. Therefore, the residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Table 14).

Seasonal Exposure Estimate
The estimated fumigant use season for the farm bin is 8 months. The residential bystander adjacent to a farm bin is anticipated to be exposed to a phosphine air concentration of 0.1 ppm 24 hr TWA for 8 months per year (Table 14).

Annual Exposure Estimate
Amortizing the seasonal exposure over the entire year, the residential bystander is estimated to be exposed to 0.07 ppm PH_3 (24 hr TWA) throughout the year (Table 14).

Commodity Fumigation in the Flat Storage Facility

Applicator

Another type of structure which was used for commodity fumigation in the registrant study was the "flat storage facility". Like the farm bins, the flat storage facilities were used for grain storage. However, these facilities were larger, with a mean volume of 405,000 cubic feet. The shapes of these structures in the registrant study were either cylindrical with conical roofs, or rectangular with peaked roofs. The exposure estimates generated in this section are for applicators, aerators, occupational bystanders, and residential bystanders potentially exposed to phosphine during fumigation and aeration of grain within the flat storage facility.

Treatment of the grain within the flat storage facility consists of fumigation followed by aeration. However, in the registrant study, only fumigation of the grain was monitored. The fumigation procedures for the flat storage facility are the same as those for the farm bin. A total of ten flat storage facilities were fumigated in the study on different days and at different sites. Nine of the fumigations were conducted using aluminum phosphide tablets and one of the fumigations was carried out using "bag blankets" which contained aluminum phosphide. However, this site was not included in estimating exposure because the phosphine levels generated by this particular formulation were substantially lower than those generated by tablets. The registrants state that the rate of phosphine generation from bag blankets is relatively low: "…the bag blankets release phosphine more slowly than most other product forms" [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. This statement is supported by the air concentration data. The mean of the breathing-zone air concentrations measured for workers handling and applying bag blankets were corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study. The resulting mean air concentration is 0.1 ppm. However, the corresponding mean for the handlers applying fumigant tablets is 13.1 ppm. Twenty-seven replicates were generated in the registrant study for the applicator fumigating commodities in flat storage facilities with tablets. For the flat storage facility, the product labels for tablet formulations instruct the user to apply the fumigant via surface application, shallow probing, deep probing or uniform addition as the flat storage is filled.

The handler's breathing-zone sampling period and the number of flat storage facilities treated per day in the study were not utilized to estimate the duration of phosphine exposure per work day. The sampling period included the steps involved in the actual fumigation (i.e., opening of fumigant container and applying fumigant) and may have also included other activities such as preparing the structure for fumigation or covering the fumigated grain in tarpaulin. The longest breathing-zone sampling period of the study for the applicators conducting commodity fumigation in the flat storage facilities is 85 minutes. The greatest number of flat storage facilities fumigated/day in the study is 4. Hence, based on the study, the greatest potential exposure period/day for handlers fumigating farm bins is 4 x 85 minutes or 340 minutes. However, a smaller work crew could be used or greater number of structures could be fumigated. Hence, the default work period of 8 hours was used to estimate short-term exposure [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

The short-term phosphine exposures to the applicator conducting commodity fumigation in the flat storage facility were estimated using the highest work shift breathing-zone phosphine air concentration. This air concentration was corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study. The work shift breathing-zone air concentration may consist of one sample or, if multiple samples were taken from the worker over the course of the work shift, the mean of these samples. For the short-term estimate, the handler is estimated to be exposed to an air concentration of 45.7 ppm for 340 minutes or 5.7 hours/day. However, greater number of structures could be fumigated. Hence, the exposure duration was assumed to be the default work period of 8 hours.

According to the product labels, in addition to aluminum phosphide tablets used in the exposure studies, the grain within the flat storage facility can also be treated with aluminum pellets, magnesium phosphide tablets, bags containing aluminum phosphide or magnesium phosphide, blister packs or polymeric fleece containing aluminum phosphide or magnesium phosphide, polyethylene strips or plates impregnated with magnesium phosphide, or, via a phosphine generator, granules containing aluminum phosphide or magnesium phosphide. Flat storage facilities can also be fumigated using cylinderized phosphine gas. Due to a lack of data, the estimates generated for the flat storage facility using tablets, and bag blankets were chosen to act as surrogate estimates for these other formulations.

Other fumigation sites listed on the product labels are the bunker, ground storage, and the silo. Due to a lack of data, the estimates generated for the flat storage facility were chosen to act as surrogate estimates for these other sites.

Short-Term Exposure Estimate

At the estimated air concentration of 45.7 ppm, the applicator would have to wear a self-contained-breathing-apparatus or SCBA. The protection factor used for SCBA is 99.99%. Hence, the handler conducting commodity fumigation in the flat storage facility using tablet or pellet formulations is anticipated to be exposed to an 8-hr TWA PH_3 air concentration of 0.005 ppm (Table 15).

Table 15. Exposure Estimates for the Applicator, Aerator, Occupational Bystander and Residential Bystander during Commodity Fumigation and Aeration in the Flat Storage Facility [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.005	0.11	0.07
aerator [f]	0.02	0.3	0.2
occupational bystander [g] (adjacent to flat storage facility during fumigation)	0.3	0.3	0.2
occupational bystander [g] (adjacent to flat storage facility during aeration)	0.3	0.3	0.2
residential bystander [h]	0.1	0.1	0.07

[a] Except for the occupational and residential bystanders, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Exposure estimates were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with a canister and 99.99% for SCBA). Due to a lack of data, the estimates generated for the flat storage facility were used as surrogate estimates for the bunker, ground storage, and silo which are also listed on some of the product labels. In addition, the exposure estimates were used as surrogate estimates for applicators, aerators, and bystanders associated with commodity fumigation in these structures using cylinderized gas and granular formulations.

[b] Short-Term Exposure: phosphine air concentration to which applicator, aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for up to one week

[c] Seasonal Exposure: phosphine air concentration to which applicator, occupational bystander, aerator, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] For the applicator exposure estimates generated in this EAD, the data set used to estimate short-term exposure for the applicator consisted of 27 replicates ranging in value from 2.4 to 45.7 ppm.

[f] The data set used to estimate short-term exposure for the aerator is a surrogate data set from the warehouse study and consisted of 10 replicates ranging in value from 0.16 to 1.2 ppm.

[g] There were no TWA breathing-zone phosphine air concentration data for the occupational bystander adjacent to the flat storage facility during application/fumigation or aeration. Hence, the 8-hr TWA PEL value of 0.3 ppm was used to estimate the short- and long-term exposures.

[h] There were no TWA breathing-zone phosphine air concentration data for the residential bystander. Hence, the 24-hr TWA equivalent of the 0.3 ppm 8-hr TWA PEL (i.e., 0.1 ppm) was used for short-term exposure. The long-term exposures were also derived from this value.

The seasonal exposure estimate was generated using the mean of the work shift breathing-zone air concentrations. These air concentrations were corrected for recovery if less than 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study.

Seasonal Exposure Estimate

The estimated fumigant use season for the flat storage facility is 8 months. The applicator without respiratory protection fumigating flat storage facilities is anticipated to be exposed to a PH_3 air concentration of 5.4 ppm (8 hr TWA) each day for 8 months of the year (Table 15). However, at this concentration, respiratory protection, such as a NIOSH/MSHA approved full-face gas mask-phosphine canister combination would be required. With a protection factor of 98%, the phosphine air concentration would be reduced from 5.4 ppm to 0.11 ppm.

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.07 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 15).

Aerator

No aeration step was conducted in the registrant studies for the flat storage facility. Therefore, as with the farm bins, the aerator exposure data of a registrant study on handler exposure in a fumigated cold weather tobacco warehouse was utilized as surrogate data. This structure is more similar to the flat storage facility than the other structures (i.e., box cars and bulk cars), for which aerator exposure data are available. The aeration was conducted four days after the fumigation which was conducted using polyethylene strips impregnated with magnesium phosphide. The aeration procedure consisted of opening the main doors to the warehouse and cutting the plastic barriers to the phosphine fumigant inside. Ten replicates (1 sample/replicate) were generated during this aeration step in the warehouse study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest air concentration measured was corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study. The resulting air concentration is 1.2 ppm. Assuming the aeration of flat storage facilities takes the same amount of time/day as the fumigation, the estimated short-term exposure for the commercial applicator conducting aeration is 1.2 ppm for 340 minutes/day. However, a greater number of structures could be fumigated. Hence, to be health-protective, the default work period of 8 hours was chosen as the exposure duration. The mean phosphine air concentration of these samples, corrected for recovery and adjusted to the estimated seasonal application rate for aluminum phosphide, is 0.3 ppm.

Short-Term Exposure Estimate

Short-term exposure is defined as acute exposure and exposures up to week in duration. The handler wearing respiratory protection and conducting aeration of the flat storage facility is anticipated to be exposed to an 8 hr TWA PH_3 air concentration of 0.02 ppm (Table 15).

Seasonal Exposure Estimate

The estimated fumigant use season for the flat storage facility is 8 months. The worker aerating flat storage facilities is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 15).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 15).

Occupational Bystander

As with the farm bin, no useable data was available for estimating 8-hr TWA exposure to the occupational bystander working adjacent to the flat storage facility undergoing commodity fumigation or aeration. However, as mentioned earlier, air concentration data for fumigating and aerating structures suggest that the 0.3 ppm PEL could be exceeded [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022]. As a result, to be health-protective, the assumed short-term exposure estimate for the occupational bystander working adjacent to a flat storage facility undergoing commodity fumigation or aeration is the legal maximum allowable exposure of 0.3 ppm (8 hr TWA). Any exposures beyond this level would require respiratory protection, which must reduce the 8-hr TWA exposure to 0.3 ppm or less.

Short-Term Exposure Estimate

The occupational bystander working adjacent to the flat storage facility during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8-hr TWA) each workday for up to one week (Table 15).

Seasonal Exposure Estimate

The estimated fumigant use season for the flat storage facility is 8 months. The occupational bystander working adjacent to the flat storage facility during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 15).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the occupational bystander is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 15).

Residential Bystander

The residential bystander is assumed to reside adjacent to the flat storage facility undergoing commodity fumigation or aeration. The data available to estimate potential phosphine exposure during fumigation and aeration are those previously described in the occupational bystander exposure section for the farm bin and mentioned above. Obtaining a 24-hr TWA exposure estimate from this data is not possible. Therefore, the highest legal maximum breathing-zone air concentration was used to estimate exposure. As mentioned earlier, this is the 8-hr TWA PEL of 0.3 ppm. Since the residential bystander is assumed to reside adjacent to the structure, the 24-hr TWA equivalent of the PEL (i.e. 0.1 ppm) was used to estimate the short-term and long-term exposure estimates (Table 15).

Short-Term Exposure Estimate
As stated earlier, the residential bystander is assumed to reside adjacent to the structure undergoing commodity fumigation or aeration. Therefore, the residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Table 15).

Seasonal Exposure Estimate
The estimated fumigant use season for the flat storage facility is 8 months. The residential bystander adjacent to a flat storage facility is anticipated to be exposed to a phosphine air concentration of 0.1 ppm 24 hr TWA for 8 months per year (Table 15).

Annual Exposure Estimate
Amortizing the seasonal exposure over the entire year, the residential bystander is estimated to be exposed to 0.07 ppm PH_3 (24 hr TWA) throughout the year (Table 15).

Commodity Fumigation in the Warehouse

The data used to estimate exposure was obtained from the same registrant task force study used to estimate exposure for the workers fumigating/aerating farm bins and flat storage facilities. In the study, the warehouses were described as being reinforced bolted steel construction and rectangular in shape with peaked roofs. The volumes of warehouses ranged from 400,000 to 2.4 million cubic feet with a mean value of 1.8 million cubic feet [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Unlike the farm bins and flat storage facilities, the fumigations of the warehouse were conducted using polyethylene strips imbedded with magnesium phosphide. The exposure estimates generated in this section are for handlers, occupational bystanders, and residential bystanders potentially exposed to phosphine during fumigation, aeration, and fumigant strip retrieval in 27 warehouses at 3 different sites.

The steps for fumigating commodities in the warehouse are preparation of the warehouse for fumigation, application of the fumigant, aeration of the warehouse, and retrieval of the spent fumigant strips. The work crew spent at least a day preparing the warehouses for fumigation. This step consisted of sealing the openings and placing trays on floors for holding fumigant strips, and distributing the unopened fumigant strip containing packages to each warehouse. Following the preparation step, the workers entered each warehouse and applied the fumigant, exited the structure, and then sealed the exit behind them. The actual application step took about 3-5 minutes per warehouse. The rest of the time was spent placarding the warehouse that was just treated, moving to the next warehouse, and preparing for the next application. Four days after the fumigation step, the warehouses were unsealed and aerated. The following day, once the phosphine concentrations within the warehouse dropped to safe levels, the workers entered the structure and retrieved the spent fumigant strips. The product label for this formulation instructs the user to apply the magnesium phosphide polyethylene strip (a string of 20 magnesium phosphide impregnated polyethylene plates), by opening it according-style and standing it on end in order to expose both sides of the plates.

The handler's breathing-zone sampling period and the number of warehouses treated per day in the study were not utilized to estimate the duration of phosphine exposure per work day. An estimate for each activity (application, aeration, and strip retrieval) was generated. All of the applications were conducted on one day. Twenty-seven warehouses at three different sites were treated. A breathing-zone sample was taken for each worker per site. The longest total breathing-zone sampling period for all three sites for a given worker is 282 minutes. However, under certain circumstances, the number of warehouses could exceed 27 or the number of workers conducting the application could be lower than that of the study (8 to 10 applicators). To be health protective, the exposure duration was assumed to be 8 hours, the assumed work-shift length. This duration was used to estimate short-term exposure [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

According to the product labels, in addition to the polyethylene strips imbedded with magnesium phosphide used in the exposure studies, commodity fumigation within the warehouse can also be conducted using aluminum pellets or tablets, magnesium phosphide tablets, bags containing aluminum phosphide or magnesium phosphide, blister packs or polymeric fleece containing aluminum phosphide or magnesium phosphide, polyethylene plates impregnated with magnesium phosphide, or, via a phosphine generator, granules containing aluminum phosphide or magnesium phosphide. Commodities within warehouses can also be fumigated using cylinderized phosphine gas. Due to a lack of data, the estimates generated for the warehouse using polyethylene strips imbedded with magnesium phosphide were chosen to act as surrogate estimates for these other formulations.

Other similar fumigation sites listed on the product labels are the mill, and the food processing plant. Both commodity and space fumigation can be conducted within these structures and the warehouse. Due to a lack of data, the commodity fumigation exposure estimates generated for the warehouse were chosen to act as surrogate estimates for warehouse space fumigation and both space and commodity fumigation within the mill and food processing plant.

Applicator

The short-term and intermediate-term phosphine exposures to the applicator conducting commodity fumigation in the warehouse were estimated using the highest work shift breathing-zone phosphine air concentration, and the mean of the work shift breathing-zone air concentrations, respectively. The work shift breathing-zone air concentration may consist of one sample or, if multiple samples were taken from the worker over the course of the work shift, the mean of these samples. A work shift breathing-zone air concentration for a worker was considered as being a replicate. According to this definition, 5 replicates were generated for the applicator. The short-term exposure for the applicator fumigating the warehouse was estimated using the highest measured breathing-zone air concentration, corrected for recovery if less than 90%, multiplied by the maximum product label application rate, and divided by the application rate used in the exposure study. The estimated air concentration for short-term exposure is 2 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if less than 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.6 ppm. This value was used to estimate seasonal exposure.

Short-Term Exposure Estimate

Short-term exposure is defined as acute exposure and exposures up to week in duration. The applicator wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination and conducting commodity fumigation in the warehouse is anticipated to be exposed to a PH_3 air concentration of 0.04 ppm (8 hr TWA) each workday for up to one week (Table 16).

Table 16. Exposure Estimates for the Applicator, Aerator, Retriever, Occupational Bystander, and Residential Bystander during Commodity Fumigation and Aeration in the Warehouse [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.04	0.01	0.007
aerator [f]	0.02	0.3	0.2
spent fumigant retriever [g]	0.01	0.12	0.08
occupational bystander (adjacent to warehouse during fumigation) [h]	0.3	0.3	0.2
occupational bystander (adjacent to warehouse during aeration) [h]	0.3	0.3	0.2
residential bystander [i]	0.1	0.1	0.07

[a] Except for the and occupational and residential bystanders, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Exposure estimates were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Due to a lack of data, the exposure estimates generated for commodity fumigation and aeration in the warehouse were used as surrogate estimates for space fumigation of the warehouse and commodity and space fumigation for the mill, and food processing plant. In addition, the exposure estimates were used as surrogate estimates for applicator, aerator, occupational bystander, and residential bystander associated with fumigation and aeration of the warehouse, mill, and food processing plant using cylinderized phosphine gas and granular formulations. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with a canister and 99.99% for SCBA).

[b] Short-Term Exposure: phosphine air concentration to which applicator, aerator, spent fumigant retriever, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for up to one week.

[c] Seasonal Exposure: phosphine air concentration to which applicator, aerator, spent fumigant retriever, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The data set used to estimate short-term exposure for the applicator consisted of 5 replicates ranging in value from 0.5 to 2 ppm.

[f] The data set used to estimate short-term exposure for the aerator consisted of 10 replicates which range in value from 0.16 to 1.2 ppm.

[g] The data set used to estimate short-term exposure for the retriever consisted of 6 replicates ranging in value from 0.18 to 0.5 ppm

[h] There were no TWA breathing-zone phosphine air concentration data for the occupational bystander adjacent to the flat storage facility during application/fumigation or aeration. Hence, the 8-hr TWA PEL value of 0.3 ppm was used to estimate the short- and intermediate-term exposures.

[i] There were no TWA breathing-zone phosphine air concentration data for the residential bystander. Hence, the 24-hr TWA equivalent of the 0.3 ppm 8-hr TWA PEL (i.e., 0.1 ppm) was used for short-term exposure. The intermediate-term exposure air concentration was also derived from this value.

Seasonal Exposure Estimate

The estimated fumigant use season for the warehouse is 8 months. The applicator wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination and conducting commodity fumigation in the warehouse is anticipated to be exposed to a PH_3 air concentration of 0.01 ppm (8 hr TWA) each workday for 8 months annually (Table 16).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the applicator is estimated to be exposed to 0.007 ppm PH_3 (8 hr TWA) throughout the year (Table 16).

Aerator

The aeration was conducted four days after the fumigation. The first step in aeration consisted of opening the main doors to the warehouse and cutting the plastic barriers to the phosphine fumigant inside. The greatest daily total time spent by a worker aerating warehouses was 210 minutes. However, the task was carried out by 9 workers. If more structures needed aerating or fewer workers were available, then the exposure duration may extend to 8 hours. Hence, to be health-protective, the exposure time was assumed to be the default work period of 8 hours. Ten replicates were generated during this aeration step in the warehouse study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest air concentration measured was corrected for recovery if less than 90%, adjusted to the maximum application rate, and subsequently divided by the application rate used in the exposure study. The estimated air concentration is 1.2 ppm. For estimating seasonal exposure, the measured breathing-zone air concentrations were corrected for recovery if less than 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study. The mean of these estimated air concentrations is 0.3 ppm.

<u>Short-Term Exposure Estimate</u>
Short-term exposure is defined as acute exposure and exposures up to week in duration. The handler wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination and conducting aeration of the warehouse is anticipated to be exposed to an 8-hr TWA PH_3 air concentration of 0.02 ppm (Table 16).

<u>Seasonal Exposure Estimate</u>
The fumigant use season for the warehouse was estimated to be 8 months. The aerator is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 16).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the aerator is anticipated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 16).

Retriever

Two days after the aeration step, the handlers retrieved the spent fumigant strips. Half of the crew of 8 to 10 workers retrieved the strips while the remainder of the workers collected the trays and fumigant strip wrappers. The longest breathing-zone sampling period was 251 minutes. However, if more structures needed to be cleaned or fewer workers were available, the exposure duration may extend to 8 hours. Six replicates were generated during the strip retrieval step in the warehouse study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest air concentration measured, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study is 0.5 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.12 ppm.

Short-Term Exposure Estimate

The handler wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination and retrieving spent fumigant strips from the warehouse is anticipated to be exposed to an 8-hr TWA PH_3 air concentration of 0.01 ppm (Table 16).

Seasonal Exposure Estimate

The fumigant use season for the warehouse was estimated to be 8 months. The retriever is anticipated to be exposed to a PH_3 air concentration of 0.12 ppm (8 hr TWA) each day for 8 months of the year (Table 16).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the retriever is estimated to be exposed to 0.08 ppm PH_3 (8 hr TWA) each day throughout the year (Table 16).

Occupational Bystander

As with the farm bin and flat storage facility, no useable data was available for estimating an 8-hr TWA exposure to the occupational bystander working adjacent to the warehouse undergoing commodity fumigation or aeration. However, as mentioned earlier, air concentration data for fumigating and aerating structures suggest that the 0.3 ppm PEL could be exceeded [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022]. As a result, the assumed short-term exposure estimate for the occupational bystander working adjacent to a warehouse undergoing commodity fumigation or aeration is the legal maximum allowable exposure of 0.3 ppm (8 hr TWA) as stated on the product labels. Any exposures beyond this level would require respiratory protection, which must reduce the 8-hr TWA exposure to 0.3 ppm or less.

Short-Term Exposure Estimate

The occupational bystander working adjacent to the warehouse during fumigation or aeration is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each workday for up to one week (Table 16).

Seasonal Exposure Estimate

The fumigant use season for the warehouse was estimated to be 8 months. The occupational bystander is anticipated to be exposed to a PH_3 air concentration of 0.3 ppm (8 hr TWA) each day for 8 months of the year (Table 16).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the occupational bystander is estimated to be exposed to 0.2 ppm PH_3 (8 hr TWA) each day throughout the year (Table 16).

Residential Bystander

The residential bystander is assumed to reside adjacent to the warehouse undergoing commodity fumigation or aeration. The data available to estimate potential phosphine exposure during fumigation and aeration are those previously described in the occupational bystander exposure section for the farm bin, and flat storage facility, and warehouse. Obtaining a 24-hr TWA exposure estimate from this data is not possible. Therefore, the highest legal maximum breathing-zone air concentration was used to estimate exposure. As mentioned earlier, this is the 8-hr TWA PEL of 0.3 ppm. Since the residential bystander is assumed to reside adjacent to the structure, the 24-hr TWA equivalent of the PEL (i.e. 0.1 ppm) was used to estimate the short-term and intermediate-term exposure estimates.

Short-Term Exposure Estimate

As stated earlier, the residential bystander is assumed to reside adjacent to the warehouse undergoing commodity fumigation or aeration. Therefore, the residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Table 16).

Seasonal Exposure Estimate

The fumigant use season for the warehouse was estimated to be 8 months. The residential bystander is anticipated to be exposed to a PH_3 air concentration of 0.1 ppm (8 hr TWA) each day for 8 months of the year (Table 16).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the residential bystander is estimated to be exposed to 0.07 ppm PH_3 (24 hr TWA) throughout the year (Table 16).

Commodity Fumigation in Rail Cars

The data used to estimate exposure for handlers and bystanders associated with rail car fumigation and aeration were obtained from the same registrant task force study used to estimate exposure for the workers fumigating/aerating commodity in farm bins, flat storage facilities, and warehouses. In the study, the box cars were described as having volumes ranging between 4500 to 6000 cubic feet. The bulk cars were described as having volumes of 4100 and 4600 cubic feet [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The exposure estimates generated in this section were derived from breathing-zone phosphine air concentration data obtained during the fumigation of 21 bulk cars and 29 box cars, and during the aeration of 3 bulk cars and 1 box car. The monitoring studies were conducted at 4 sites. One site consisted of a grain-elevator while the three other sites were cereal processing and packaging plants. Five bulk cars were fumigated outside of the grain-elevator while both bulk cars and box cars were fumigated and aerated both inside and outside of the cereal processing and packaging plants. Breathing-zone phosphine air concentrations were obtained from the worker while fumigating or aerating each rail car. In addition, the breathing-zones of occupational bystanders assisting the fumigators or aerators were obtained. Finally, the breathing-zone phosphine air concentrations of occupational bystanders which were "nearby" the rail cars but not associated with the fumigation or aeration were measured. These workers drove forklifts, operated palletizers, or filled bags with finished product at a packaging line within the cereal processing and packaging plants.

Short-term exposure for the applicator fumigating and aerating rail cars was estimated using the highest work shift breathing-zone air concentration. The work shift breathing-zone air concentration may consist of one sample or, if multiple samples were taken from the worker over the course of the work shift, the mean of these samples. The measured breathing-zone air samples were corrected for recovery if less than 90% and adjusted to the maximum application rate. Intermediate-term phosphine exposure to the applicator conducting commodity fumigation in the rail car was estimated using the mean of the work shift breathing-zone air concentrations adjusted to the estimated seasonal application rate for aluminum phosphide and corrected for recovery if less than 90%.

A work shift breathing-zone air concentration for a worker was considered as being a replicate. According to this definition, 12 replicates were generated for the bulk car fumigator, and 17 replicates for the box car fumigator. In addition, one replicate was generated for an "assistant applicator" that assisted in the box car fumigation. The breathing-zone air concentration datum from the assistant applicator was combined with breathing-zone air concentration data of the box car fumigator. Nine replicates were generated for the "assistant worker" who assisted in the fumigation of the bulk car. This "handler" did not handle the fumigant but would act as a safety observer, placard the car after fumigation, or monitor the area for phosphine. One replicate was generated for the assistant worker during the fumigation of box cars. Two replicates were generated for the "nearby worker" which was an occupational bystander who drove a forklift, or operated a palletizer inside of the plant and near the bulk cars after application of the fumigant but before aeration of the bulk car. Fourteen replicates were generated for the nearby worker in the plant during application of the fumigant to the box cars. Nine replicates were generated for the nearby worker after application of the fumigant to the box cars. For aeration of bulk cars, three replicates were obtained for the aerator and one replicate for the assistant aerator who would open the hatches on the bulk car following fumigation but would not retrieve the spent fumigant from within the car. One replicate was generated for the nearby worker during bulk car aeration. Three replicates were generated for the nearby worker after aeration of the bulk car. Monitoring studies were conducted for the box car aeration inside and outside of the plant. Only one replicate was obtained for the aerator during aeration inside of the plant. After this aeration, one replicate was generated for a nearby worker. For the outdoor aeration, one replicate was generated for the aerator, and two for the assistant aerator. Finally, the breathing-zones of the "packaging line for consumer products" workers that filled bags with the cereal which had been fumigated were monitored. The cereal was fumigated and then transferred via "several pneumatic and gravity transfers to holding tanks prior to packaging". This worker was monitored at the cereal processing and packaging plant, but was not associated with any particular bulk or box car fumigation or aeration. The exposure estimates for this worker were presented along with the applicator, aerator, occupational bystander, and residential bystander exposure estimates for bulk car and box car fumigation and aeration. Seven replicates were generated for the packaging line for consumer products workers.

Paper bags containing aluminum phosphide or magnesium phosphide were used to fumigate the rail cars. The “gas bags” were placed in cardboard holders called “Fumi-Discs” or “Fumi-Boards”, which were placed within the car. In addition, some of the bulk cars were fumigated with Phostoxin Pellet Prepacs which consisted of a clear plastic blister strip filled with a total of 165 aluminum phosphide pellets and covered with a gas-permeable fleece. The applicator would remove the fumigant from the container, place it in the cardboard holder, and then secure the cardboard holder to a bulkhead within the box car or place the fumigant holder underneath a hatch on the top of the bulk car. The door or hatch was then closed and sealed. The applicator would then placard the box or bulk car being fumigated. Alternatively, the “assistant worker” could placard the rail car and help seal the hatches (bulk car) or doors (box car) [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. These application procedures are essentially the same as those described in the current product labels for these formulations.

According to the product labels, in addition to the aluminum phosphide and magnesium phosphide gas bags used in the exposure studies, the rail cars can also be treated with aluminum phosphide tablets or pellets, magnesium phosphide tablets, polymeric fleece containing aluminum phosphide, polyethylene plates impregnated with magnesium phosphide, or, via a phosphine generator, granules containing aluminum phosphide or magnesium phosphide. Rail cars can also be fumigated using cylinderized phosphine gas. Due to a lack of data, the exposure estimates generated for the rail cars using aluminum phosphide and magnesium phosphide gas bags, and blisters containing aluminum phosphide pellets were chosen to act as surrogate estimates for these other formulations.

Other similar fumigation sites listed on the product labels are the storage container, and vehicle (i.e., car, van, truck). Due to a lack of data, the estimates generated for the box cars were chosen to act as surrogate estimates for these other sites.

Bulk Car Fumigation and Aeration

Applicator

The highest work shift breathing-zone phosphine air concentration corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study for the applicator fumigating bulk cars is 2 ppm. The mean sampling period for this scenario is 22 minutes. However, due to a lack of data, the 8-hr TWA air concentration for estimating short-term exposure was assumed to be 2 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.4 ppm. This value was used to estimate seasonal and annual exposure.

Short-Term Exposure Estimate

The handler wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination while fumigating rail cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.04 ppm (Table 17).

Table 17. Commodity Fumigation and Aeration in the Bulk Car Exposure Estimates for the Applicator, Aerator, Occupational Bystander, and Residential Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.04	0.008	0.005
assistant worker [f]	0.02	0.2	0.13
occupational bystander [g] (nearby worker: post-application/pre-aeration)	0.007	0.1	0.07
aerator [h]	0.08	0.02	0.01
assistant aerator [i]	0.12	0.12	0.08
occupational bystander [j] (nearby worker: post-aeration)	0.009	0.2	0.13
occupational bystander [k] (packaging line for consumer products worker)	0.08	0.2	0.13
residential bystander [l]	0.1	0.1	0.07

[a] Except for the residential bystander, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Exposure estimates were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Due to a lack of data, the exposure estimates generated for commodity fumigation and aeration in the bulk car were chosen to be used as surrogate estimates for the applicator, aerator, occupational bystander, and residential bystander associated with fumigation and aeration of the bulk car using cylinderized phosphine gas and granular formulations. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with a canister and 99.99% for SCBA).

[b] Short-Term Exposure: phosphine air concentration to which applicator, aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day and 24 hr TWA/day, respectively, for up to one week. [c c]

[c] Seasonal Exposure: phosphine air concentration s to which applicator, aerator, occupational bystander, and residential bystanders are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The “applicator” would remove the fumigant from the container, place it in the cardboard holder, and then place the fumigant holder underneath a hatch on the top of the bulk car. The data set used to estimate short-term exposure for this scenario consisted of 12 replicates ranging from 0.35 to 2 ppm.

[f] The “assistant worker” assisted in the fumigation of the bulk car. This occupational bystander did not handle the fumigant but would act as a safety observer, placard the car after fumigation, or monitor the area for phosphine. The data set for estimating short-term exposure for this scenario consisted of nine replicates which ranged in value from 0.15 to 1 ppm.

[g] The “nearby worker” was an occupational bystander who drove a forklift, or operated a palletizer inside of the plant and near the fumigating or aerating bulk cars. In this instance, the worker was sampled post-application but before aeration. The data set for estimating short-term exposure for this scenario consisted of 2 replicates which ranged from 0.23 to 0.35 ppm.

[h] The “aerator” would retrieve the spent fumigant from the bulk car. The data set for estimating short-term exposure for this scenario consisted of 3 replicates ranging in value from 1.7 to 4.2 ppm.

[i] The “assistant aerator” would open the hatch on the bulk to initiate aeration but would not retrieve the spent fumigant. The data set for estimating short-term exposure for this scenario consisted of 1 replicate equal to 5.8 ppm.

[j] The “nearby worker” was an occupational bystander who drove a forklift, or operated a palletizer inside of the plant and near the fumigating or aerating bulk cars. In this instance, the worker was sampled post-aeration. The data set for estimating short-term exposure for this scenario consisted of 1 replicate equal to 0.43 ppm.

[k] The packaging line for consumer products worker would package cereal in the cereal processing and packaging facility and was potentially exposed to phosphine fumes from both bulk car and box car fumigation and aeration. Moreover, exposure to phosphine emitted by the fumigated cereal being handled by the worker may have occurred. The data set for estimating short-term exposure for this scenario consisted of 7 replicates ranging from 0.02 to 3.8 ppm.

[l] The residential bystander was assumed to reside adjacent to the facilities with fumigating or aeration bulk car and box cars. The estimated fumigant use season is 8 months. The 24-hr TWA exposure estimates were derived from the 8-hr TWA PEL of 0.3 ppm.

Seasonal Exposure Estimate

The fumigant use season for the box car was estimated to be 8 months. The applicator wearing NIOSH/MSHA approved full-face gas mask-phosphine canister combination while fumigating rail cars is anticipated to be exposed to a phosphine air concentration of 0.008 ppm (8-hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.005 ppm phosphine (8-hr TWA) each day over the course of the year (Table 17).

Assistant Worker

The assistant worker would act as a safety observer, placard the fumigated and sealed bulk car, or take measurements of phosphine air concentrations. The highest work shift breathing-zone phosphine air concentration for the assistant worker is 1 ppm. The mean sampling period for the breathing-zone samples is 22 minutes. For estimating exposure, these concentrations were assumed to be the 8-hr TWA air concentrations for phosphine. The mean of the measured breathing-zone air concentrations, corrected for recovery and adjusted to the seasonal application rate is 0.2 ppm.

Short-Term Exposure Estimate

The handler wearing NIOSH/MSHA approved full-face gas mask-phosphine canister combination while assisting in the fumigation of bulk cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.02 ppm (Table 17).

Seasonal Exposure Estimate

The estimated fumigant use season for the bulk car is 8 months. The worker assisting in the fumigation of bulk cars is anticipated to be exposed to a phosphine air concentration of 0.2 ppm (8-hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the assistant worker is anticipated to be exposed to 0.13 ppm phosphine (8-hr TWA) each day over the course of the year (Table 17).

Occupational Bystander

For bulk car fumigation, two types of bystanders were monitored in the study. These occupational bystanders were the “nearby worker”, and “packaging line for consumer products” worker. The nearby worker, driving a forklift or operating a palletizer, was sampled post-application but before aeration, and was described as being within the general vicinity of the fumigated car. The highest work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study for the nearby worker, is 0.35 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.1 ppm. The mean sampling period for these samples is 63 minutes. For estimating exposure, these concentrations were assumed to be the 8-hr TWA air concentrations for phosphine.

Short-Term Exposure Estimate
The worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while working nearby fumigated bulk cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.007 ppm (Table 17).

Seasonal Exposure Estimate
The estimated fumigant use season for the bulk car is 8 months. The worker nearby fumigated bulk cars is anticipated to be exposed to a phosphine air concentration of 0.1 ppm (8 hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate
Amortizing the seasonal exposure over the entire year, the nearby worker is anticipated to be exposed to 0.07 ppm phosphine (8 hr TWA) each day over the course of the year (Table 17).

The next type of occupational bystander is the “packaging line for consumer products” worker. The highest work shift breathing-zone phosphine air concentration for this worker, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, is 3.8 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.2 ppm. The mean sampling period for these samples is 148 minutes. For estimating exposure, these concentrations were assumed to be the 8-hr TWA air concentrations for phosphine. The relatively high phosphine air concentration in the breathing-zone of this worker may be due to phosphine gas emanating from the bulk car or from the fumigated commodity being packaged.

Short-Term Exposure Estimate
The packaging line for consumer products worker wearing a NIOSH/MSHA approved full-face gas mask-phosphine canister combination is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.08 ppm (Table 17).

Seasonal Exposure Estimate
The estimated fumigant use season for the bulk car is 8 months. This packaging line for consumer products worker is anticipated to be exposed to a phosphine air concentration of 0.2 ppm (8 hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate
The annual exposure estimate for the packaging line for consumer products worker is 0.13 ppm phosphine (8-hr TWA) each day over the course of the year (Table 17).

The residential bystander was assumed to reside adjacent to the cereal processing and packaging plant where the bulk and box cars were fumigated and aerated. No TWA breathing-zone phosphine air concentration data was available for the residential bystander scenario. Hence, the 24-hr TWA equivalent of the product label 8-hr TWA PEL restriction of 0.3 ppm was utilized to estimate exposure.

Residential Bystander

<u>Short-Term Exposure Estimate</u>
As stated earlier, the residential bystander is assumed to reside adjacent to the cereal processing and packaging plant where the bulk and box cars were fumigated and aerated. The residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Table 17).

<u>Seasonal Exposure Estimate</u>
The estimated fumigant use season for the bulk car is 8 months. The residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm for 8 months annually (Table 17).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure air concentration over the year, the residential bystander is anticipated to be exposed to 0.07 ppm PH_3 (24-hr TWA) (Table 17).

Aerator

Aeration of the bulk cars was conducted in an indoor rail dock area of a cereal processing and packaging plant. The highest work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the aerator is 4.2 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 1 ppm. The mean sampling period is 21 minutes. Although the exposures would likely be sporadic, to be health protective the 8-hr TWA air concentrations were assumed to be 4.2 ppm and 1 ppm, for estimating short-term and intermediate-term exposures, respectively.

<u>Short-Term Exposure Estimate</u>
The worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while aerating bulk cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.08 ppm (Table 17).

<u>Seasonal Exposure Estimate</u>
The estimated fumigant use season for the bulk car is 8 months. The worker wearing a full-face respirator while aerating bulk cars is anticipated to be exposed to a phosphine air concentration of 0.02 ppm (8 hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the aerator is anticipated to be exposed to 0.01 ppm phosphine (8-hr TWA) each day over the course of the year (Table 17).

Assistant Aerator

The assistant aerator is a "handler" that opens the hatches of the bulk car to aerate the commodity. However, the worker does not retrieve the fumigant. Only one work shift breathing-zone phosphine air concentration was generated for the assistant aerator. This air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, is 5.8 ppm. The sampling period was 36 minutes. For estimating exposure, this concentration was assumed to be the 8-hr TWA air concentration for phosphine. This air concentration was used to estimate both short-term and intermediate-term exposures.

Short-Term Exposure Estimate

The handler wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while assisting in the aeration of fumigated bulk cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.12 ppm (Table 17).

Seasonal Exposure Estimate

The estimated fumigant use season for the bulk car is 8 months. The worker wearing a full-face respirator and assisting in the aeration of bulk cars is anticipated to be exposed to a phosphine air concentration of 0.12 ppm (8 hr TWA) each day for 8 months of the year (Table 17).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the assistant aerator is anticipated to be exposed to 0.08 ppm phosphine (8 hr TWA) each day annually (Table 17).

Occupational Bystander

One type of occupational bystander associated with bulk car aeration is the nearby worker. This worker, driving a forklift or operating a palletizer, was sampled post-aeration and was described as being within the general vicinity of the bulk car. The only work shift breathing-zone phosphine air concentration generated for the nearby worker, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, is 0.43 ppm. Following correction for recovery if < 90%, multiplication by the estimated seasonal application rate for aluminum phosphide, and division by the application rate used in the exposure study, this value becomes 0.2 ppm. The mean sampling period for the two samples making up the work shift breathing-zone air concentrations is 157 minutes. For estimating short- and long-term exposures, 0.43 ppm and 0.2 ppm, respectively, were assumed to be the 8-hr TWA air concentration for phosphine.

<u>Short-Term Exposure Estimate</u>
The worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while nearby fumigated bulk cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.009 ppm (Table 17).

<u>Seasonal Exposure Estimate</u>
The estimated fumigant use season for the bulk car is 8 months. The worker nearby fumigated bulk cars is anticipated to be exposed to a phosphine air concentration of 0.2 ppm (8 hr TWA) each day for 8 months of the year (Table 17).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the nearby worker is anticipated to be exposed to 0.13 ppm phosphine (8 hr TWA) each day over the course of the year (Table 17).

Another occupational bystander associated with bulk car aeration is the packaging line for consumer products worker. This worker could potentially be exposed to phosphine released from the bulk car during fumigation or aeration. Another source of phosphine gas could be from the fumigated commodity being packaged. Due to a lack of data, the previously described exposure estimates for this bystander scenario for bulk car fumigation were also utilized for bulk car aeration (Table 17).

Box Car Fumigation and Aeration

The highest work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the applicator is 4 ppm. The mean of the work shift breathing-zone phosphine air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.5 ppm. The mean sampling period for this scenario is 14 minutes. However, due to a lack of data, the 8-hr TWA air concentration for estimating short-term exposure was assumed to be 4 ppm. The corresponding 8-hr TWA for estimating intermediate-term exposure is 0.5 ppm.

The box car fumigation procedures were similar to those of the bulk car. The box car fumigations at the three cereal processing and packaging plants were initiated within the indoor rail dock within the plants. The fumigant-containing box cars were then sealed and moved outside of the building into the switching yard for the remainder of the fumigation.

Applicator

<u>Short-Term Exposure Estimate</u>
The handler wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while fumigating box cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.08 ppm (Table 18).

Table 18. Commodity Fumigation in the Box Car: Exposure Estimates for the Applicator, Occupational Bystander, and Residential Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.08	0.01	0.007
assistant worker [f]	0.02	0.008	0.005
occupational bystander [g] (nearby worker: application)	0.03	0.3	0.2
occupational bystander [h] (nearby worker: post-application)	0.05	0.3	0.2
residential bystander [i]	0.1	0.1	0.07

[a] Except for the residential bystander, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Exposure estimates were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Due to a lack of data, the estimates generated for the box cars were chosen to be used as surrogate estimates for the storage container, and vehicle (i.e., car, van, truck) which are also listed on some of the product labels. In addition, the exposure estimates were chosen to be used as surrogate estimates for the applicator, aerator, occupational bystander, and residential bystander associated with fumigation and aeration of the box car using cylinderized phosphine gas or granular formulations. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with canister and 99.99% for SCBA).

[b] Short-Term Exposure: phosphine air concentration to which applicator, aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for up to one week.

[c] Seasonal Exposure: phosphine air concentration to which applicator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The "applicator" would remove the fumigant from the container, place it in the cardboard holder, and then secure the cardboard holder to a bulkhead within the box car. The data set used to estimate short-term exposure for this scenario consisted of 17 replicates ranging from 0.12 to 4 ppm.

[f] The "assistant worker" assisted in the fumigation of the box car. This occupational bystander did not handle the fumigant but would act as a safety observer, placard the car after fumigation, or monitor the area for phosphine. The data set used to estimate short-term exposure for this scenario consisted of 1 replicate equal to 1 ppm.

[g] The "nearby worker" was an occupational bystander who drove a forklift, or operated a "palletizer" inside of the plant and near the box car during application of fumigant. The data set used to estimate short-term exposure for this scenario consisted of 14 replicates ranging from 0.2 to 1.7 ppm.

[h] The “nearby worker” was monitored after fumigant application but before aeration. The data set used to estimate short-term exposure for this scenario consisted of 9 replicates ranging from 0.04 to 2.5 ppm.

[i] The residential bystander was assumed to reside adjacent to the facilities with fumigating or aerating bulk car or box cars.

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months. The applicator wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.01 ppm.

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the applicator is anticipated to be exposed to 0.007 ppm phosphine (8 hr TWA) each day over the course of the year (Table 18).

The assistant worker was a handler who would act as a safety observer, placard the fumigated and sealed box car, or take measurements of phosphine air concentrations. Only 1 replicate was generated for this worker scenario. The work shift breathing-zone air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the assistant worker was 1 ppm. In contrast, the air concentration corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study is 0.4 ppm. The mean of the sampling periods for the two samples making up the replicate is 11 minutes. For estimating exposure, these concentrations were assumed to be the short-term and seasonal, respectively, 8-hr TWA air concentrations for phosphine.

Short-Term Exposure Estimate

The worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while assisting in the fumigation of box cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.02 ppm (Table 18).

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months The assistant worker wearing respiratory protection is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.008 ppm (Table 18).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the assistant worker is anticipated to be exposed to 0.005 ppm phosphine (8 hr TWA) each day over the course of the year (Table 18).

Occupational Bystander Exposure to Phosphine due to Fumigant Application

The type of occupational bystander associated with box fumigation in the study was the “nearby worker”. This worker, driving a forklift or operating a palletizer, was described as being within the general vicinity of the applicator and is also assumed to work in a well-ventilated area. This bystander was monitored during the application of fumigant and after application but before aeration. During application, the highest work shift breathing-zone phosphine air concentration corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the assistant worker is 1.7 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.3 ppm. The mean sampling period is 59 minutes. Exposure to these air concentrations would coincide with fumigant application and, therefore, likely be episodic. However, to be health protective, these concentrations were assumed to be the 8-hr TWA air concentrations for phosphine.

Short-Term Exposure Estimate

The nearby worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination during the fumigation of box cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.03 ppm (Table 18).

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months. The nearby worker is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.3 ppm for 8 months annually (Table 18).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the assistant worker is anticipated to be exposed to 0.2 ppm phosphine (8 hr TWA) each day over the course of the year (Table 18).

For the post-application nearby worker, the highest work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, is 2.5 ppm. The mean of the measured breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.3 ppm. The mean sampling period is 94 minutes. Compared to the assumed work period of 8 hours, the sampling time is relatively short. However, due to a lack of data, these concentrations were assumed to be the 8-hr TWA air concentrations for phosphine.

Short-Term Exposure Estimate

The nearby worker wearing respiratory protection during the fumigation of box cars is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.03 ppm (Table 18).

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months. The post-application nearby worker is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.3 ppm for 8 months annually (Table 18).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the post-application nearby worker is anticipated to be exposed to 0.2 ppm phosphine (8 hr TWA) each day over the course of the year (Table 18).

Fumigated box cars were aerated at two of the cereal processing and packaging plant sites in the study. The cars were aerated outside of the plant, in the switching yard, at one site (Site D), while the aeration was conducted in an "isolated area of the facility" at the other site (Site E). There was one replicate each for the aerator and two assistant aerators at Site D. There was one replicate for the aerator at Site E. To aerate the box car, the aerator or assistant aerator, using respiratory protection, opened the door about 1 foot and took an air sample using a length-of-stain dosimeter or electrochemical detector. The aerator then opened the door completely and entered the car to retrieve and dispose the spent fumigant. The car was allowed to aerate completely. In the registrant study, the box cars were said to have generally taken less than 10 minutes (Site E) or 15 minutes (Site D) to aerate enough for unloading. The work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the aerator at Site D is 2.8 ppm (one sample). The measured air concentration, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 1 ppm. The sampling period is 13 minutes. The work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the aerator at Site E (indoor aeration) was 4.9 ppm (one sample). The sampling period is 4 minutes. The measured phosphine air concentration, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 2 ppm. Although the sampling times are relatively short and the potential exposures may be sporadic, occurring only when aerations were conducted, due to a lack of data, these air concentrations were assumed to be 8-hr TWA's.

Aeration of Box Car Outside of Facility

Aerator

<u>Short-Term Exposure Estimate</u>
The worker wearing respiratory protection and aerating box cars outdoors is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.06 ppm (Table 19).

Table 19. Commodity Aeration in the Box Car: Exposure Estimates for the Aerator, Occupational Bystander, and Residential Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
aerator (outdoor) [e]	0.06	0.02	0.013
aerator (indoor) [e]	0.1	0.04	0.03
assistant aerator (outdoor aeration) [f]	0.01	0.17	0.11
occupational bystander [g] (nearby worker: indoor post-aeration)	0.05	0.02	0.01
occupational bystander [h] (packaging line for consumer products worker)	0.08	0.2	0.13
residential bystander [i]	0.1	0.1	0.07

[a] Except for the residential bystander, the exposure estimates generated in this table are from breathing-zone air concentrations which have been multiplied by the maximum product label application rate/application rate used in the exposure study (short-term exposure) or the estimated seasonal application rate for aluminum phosphide/application rate used in the exposure study (seasonal and annual exposure), and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Due to a lack of data, the estimates generated for the box cars were chosen to act as surrogate estimates for the storage container, and vehicle (i.e., car, van, truck) which are also listed on some of the product labels. In addition, the exposure estimates were chosen to act as surrogate estimates for the applicator, aerator, occupational bystander, and residential bystander associated with fumigation and aeration of the box car using cylinderized phosphine gas or granular formulations. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with canister and 99.99% for SCBA).

[b] Short-Term Exposure: phosphine air concentration to which aerator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for up to one week.

[c] Seasonal Exposure: phosphine air concentration to which applicator, occupational bystander, and residential bystander are exposed to for 8 hr TWA/day, 8 hr TWA/day, and 24 hr TWA/day, respectively, for a season of 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The "aerator" would retrieve the spent fumigant from the box car. The data set used to estimate short-term exposure for the outdoor aerator scenario consisted of 1 replicate equal to 2.8 ppm. The data set used to estimate exposure for the indoor aerator consisted of 1 replicate equal to 4.9 ppm.

[f] The "assistant aerator" would open the door on the box car to initiate aeration but did not retrieve the spent fumigant. The data set used to estimate short-term exposure for this scenario consisted of 2 replicates ranging from 0.4 to 0.5 ppm.

[g] The "nearby worker" was an occupational bystander who drove a forklift, or operated a "palletizer" inside of the plant and near the boxcar after indoor aeration. The data set used to estimate short-term exposure for this scenario consisted of 1 replicate which is equal to 2.3 ppm.

[h] The "packaging line worker" would package cereal in the cereal processing and packaging facility and was potentially exposed to phosphine fumes from handling fumigated cereal, and from bulk car and box car fumigation and aeration. The "nearby worker" was an occupational bystander who drove a forklift, or operated a "palletizer" inside of the plant and near the box car during application of fumigant. The data set used to estimate short-term exposure for this scenario consisted of 7 replicates ranging from 0.02 to 3.8 ppm.

[i] The residential bystander was assumed to reside adjacent to the facilities with fumigating or aeration bulk car and box cars.

Seasonal Exposure Estimate
The estimated fumigant use season for the box car is 8 months. The worker aerating boxcars outdoors is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.02 ppm for 8 months annually (Table 19).

Annual Exposure Estimate
The outdoor aerator is anticipated to be exposed to 0.03 ppm phosphine (8-hr TWA) each day annually (Table 19).

Aeration of Box Car Inside of Facility

Aerator
Short-Term Exposure Estimate
Short-term exposure is defined as acute exposure and exposures up to week in duration. The worker wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination and aerating box cars indoors is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.1 ppm (Table 19).

Seasonal Exposure Estimate
The estimated fumigant use season for the box car is 8 months. The worker aerating box cars indoors is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.04 ppm for 8 months annually (Table 19).

Annual Exposure Estimate
The indoor aerator is anticipated to be exposed to 0.03 ppm phosphine (8 hr TWA) each day annually (Table 19).

Two assistant aerators helped aerate the box car at Site D. The two assistant aerators were exposed to phosphine air concentrations, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, of 0.4 ppm and 0.5 ppm (1 sample/assistant aerator). The higher of the two values was used to estimate short-term exposure. The air concentration, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.17 ppm. This value was used to estimate seasonal and annual exposures. The sampling period for each worker was 13 minutes.

Assistant aerator
Short-Term Exposure Estimate
The assistant aerator is estimated to be exposed to a phosphine air concentration of 0.01 ppm 8 hours TWA (Table 19).

Seasonal Exposure Estimate
The estimated fumigant use season for the box car is 8 months. The assistant aerator is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.17 ppm for 8 months annually (Table 19).

Annual Exposure Estimate

The assistant aerator is anticipated to be exposed to 0.11 ppm phosphine (8 hr TWA) each day annually (Table 19).

Occupational Bystander Exposure to Phosphine due to Aeration

One type of occupational bystander was present during and after the box car aerations. This bystander was the "nearby worker" who was present after the box car aeration procedure at Site E. The "nearby worker" occupational bystander was monitored after the indoor aeration procedure at Site E and had a breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, of 2.3 ppm (1 sample). The measured breathing-zone air concentration, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.9 ppm. The sampling period for this worker was 45 minutes. Although the sampling times are relatively short, due to a lack of data, these air concentrations were assumed to be 8-hr TWA's.

Nearby Worker

Short-Term Exposure Estimate

The nearby worker is anticipated to be exposed to an 8-hr TWA PH_3 air concentration of 0.05 ppm (Table 19).

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months. The nearby worker is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.02 ppm for 8 months annually (Table 19).

Annual Exposure Estimate

The nearby worker is anticipated to be exposed to 0.01 ppm phosphine (8 hr TWA) each day annually (Table 19).

Occupational Bystander Exposure: Packaging Line Worker

As mentioned earlier, an occupational bystander who may potentially be exposed to phosphine fumes from either fumigation or aeration of rail cars and packaging of fumigated cereal is the packaging line worker. This employee packages the finished cereal product which is fumigated and then transferred to various holding tanks prior to packaging. In the registrant study, the breathing-zone air concentration of this worker was monitored for phosphine after the aeration of bulk or box cars. The bulk cars were aerated in the indoor rail dock. The box cars were aerated either outside in the switching yard or inside the plant at an "isolated area of the facility". The type or location of aeration was not listed in the study for this occupational bystander. Moreover, the amount of time between sample collection and the end of the aeration was not listed. The breathing-zones of packaging line workers were sampled at Sites D and E. Where the workers were located relative to the indoor aerations was not reported. There were seven replicates generated for the packaging line worker from both sites. The highest work shift breathing-zone phosphine air concentration, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, for the packaging line worker is 3.8 ppm. The mean of the work shift breathing-zone phosphine air concentrations, corrected for recovery if < 90%, multiplied by the estimated seasonal application rate for aluminum phosphide, and divided by the application rate used in the exposure study, is 0.2 ppm. The mean sampling time of the 7 replicates is 148 min with the highest air concentration of 3.8 ppm having the shortest sample time of 49 minutes. As mentioned earlier, the cereal which the workers were packaging had been fumigated previously and had undergone several transfers to holding tanks before being packaged. Hence, the one high breathing-zone reading is potentially due to this grain not being fully aerated prior to being handled and not due to fumigation or aeration of the bulk or box cars. As with the other samples, the sampling period is substantially shorter than the assumed work period of 8 hours.

Short-Term Exposure Estimate

The packaging line worker wearing respiratory protection during the fumigation of box cars is anticipated to be exposed to an 8-hr TWA PH_3 air concentration of 0.08 ppm (Tables 19).

Seasonal Exposure Estimate

The estimated fumigant use season for the box car is 8 months. The packaging line worker is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.2 ppm for 8 months annually (Table 19).

Annual Exposure Estimate

The packaging line worker is anticipated to be exposed to 0.13 ppm phosphine (8 hr TWA) each day annually (Table 19).

Residential Bystander Exposure to Phosphine from Bulk Car and Box Car Fumigation and Aeration

The residential bystander is assumed to reside adjacent to the grain-elevator complex or cereal processing and packaging plant where rail cars are undergoing commodity fumigation or aeration. The data available to estimate potential phosphine exposure during fumigation and aeration are those previously described in the occupational bystander exposure section for the bulk car and box car fumigations and aerations mentioned above. Obtaining a 24-hr TWA exposure estimate for the residential bystander from this data is not possible. Therefore, due to a lack of data, the highest legal maximum breathing-zone air concentration was used to estimate exposure. As mentioned earlier, this is the 8-hr TWA PEL of 0.3 ppm. Since the residential bystander is assumed to reside adjacent to the structure, the 24-hr TWA equivalent of the PEL (i.e. 0.1 ppm) was used to estimate the short-term and long-term exposure estimates.

Short-Term Exposure Estimate

As stated earlier, the residential bystander is assumed to reside adjacent to the structure containing bulk or box cars undergoing fumigation or aeration. Therefore, the residential bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Tables 19).

Seasonal Exposure Estimate
The estimated fumigant use season for the box car is 8 months. The residential bystander is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.1 ppm for 8 months annually (Table 19).

Annual Exposure Estimate
The residential bystander is estimated to be exposed to 0.07 ppm PH_3 (24 hr TWA) annually (Table 19).

Commodity Fumigation on Ships

Ship Hold

Five studies were reviewed for estimating phosphine exposure to workers and residential bystanders located on ships undergoing fumigation or aeration of the grain within the holds [Phos-Fume Chemicals Co. Ltd. (1983) Registration Package Number 225-022]. These studies are presented in journal articles containing air monitoring data for a total of five ships carrying grain (e.g., corn and wheat). As described in the studies, the fumigations of the grain within the ship holds were conducted while the ships were in-transit. The fumigant used was aluminum phosphide in tablet or bag blanket formulations. After reaching the port of destination, the holds were aerated in preparation for removal of the grain. The air samples taken in the studies were instantaneous samples taken at various locations in and on the ship. The samples were taken using colorimetric tubes or a Miran IA infrared gas analyzer. The locations sampled in the studies were on deck downwind of the hold hatches during fumigant application and aeration, in the crew's living or workspaces during fumigation, and within the hold containing the fumigated or aerated grain. No personal breathing-zone TWA samples were taken in the studies. Due to a lack of data, the estimates generated for ship hold fumigation were chosen to act as surrogate estimates for commodity fumigation in the barge which is listed on some of the product labels. In addition, these estimates were chosen to act as surrogate estimates for commodity fumigation in ship holds and barges using cylinderized phosphine gas, or granular formulations.

The first of the five studies in the data volume is titled, "A Review of U.S. Research on In-Transit Shipboard Fumigation of Grain" and contained monitoring data for phosphine air concentrations in and on four bulk dry cargo vessels containing grain fumigated with "80-20 (carbon tetrachloride – carbon bisulfide liquid fumigant)", and aluminum phosphide tablets and bag blankets. The air samples were taken periodically during the application of aluminum phosphide bag blankets or tablets. The samples were taken from within the ship's three holds on the grain surface, on deck around all seven hatches, and within the ship's living and work areas. Samples were also taken on shore downwind of the hatch openings during the application of the fumigant. During transit while the grain was undergoing fumigation, the investigators sampled the air within the living and working areas of the crew. Samples were taken every 6 hours during the first 48 hours and then every 12 hours during the rest of the voyage. At the port of destination, while the grain was being unloaded, samples were taken at the surface of the grain in the hold where the workers were located and from the crew's work areas. During application, phosphine was detected downwind and immediately adjacent to the open hatches of the hold. Phosphine was also detected for a "matter of minutes" when the hatches were opened for unloading the fumigated grain. However, during both incidents, the concentration never exceeded 0.3 ppm. Phosphine was never detected in any of the living quarters. Moreover, phosphine was not detected outside of the fumigated holds while the ship was in transit. The specific application rate used in each vessel was not provided. However, the range of application rates used for the vessels was listed as 0.033 to 0.09 grams/cubic foot. If the lower of the two application rates is used to estimate the air concentrations adjusted to the maximum application rate of 0.145 grams/cubic foot, then the readings (less than 0.3 ppm), taken near the hatches during application and unloading of the fumigated grain would become 1.3 ppm. The non-detects of the study can't be adjusted to the maximum application rate. However, they would be less than 1.3 ppm [Phos-Fume Chemicals Co. Ltd. (1983) Registration Package Number 225-022].

The second study is described a journal article on phosphine air concentrations generated on board a ship during fumigant application, in-transit fumigation, and aeration of fumigated wheat. The ship was a bulk dry-cargo vessel which contained wheat undergoing fumigation in three of the holds. The wheat was fumigated using aluminum phosphide tablets which were applied via a layering method or a subsurface method. The layering technique consisted of applying 1/3 of the dose when the hold is approximately 33% full, 1/3 of the dose when the hold is about 67% of capacity, and the last third of the dose before the final 5% of the wheat was added. The subsurface method consisted of a worker walking out onto the loaded grain and stepping on the fumigant tablets placed on the surface, forcing them into the grain. During loading of the grain, in-transit, and unloading of the grain, air samples were taken from within the ship's three holds, on deck around all seven hatches, and within the ship's living and work areas. During most of the applications, "no phosphine was detected upwind at the edge of the hatch or at any other locations on deck or in the ship's living and working areas after any of the applications". However, phosphine was detected downwind and at the edge of the hatch from 5 to 20 minutes after each application. After 30 minutes, phosphine was either not detected or was below 0.1 ppm. Moreover, for one of the applications, increased phosphine levels were caused by delays during the application step. During the delays, workers closed the hatches to the holds which allowed the phosphine levels to increase within the hold. When the hatches were opened to continue the application, phosphine was detected near the edge of the hatches but rapidly dissipated. The highest readings were 7 ppm detected for 1 to 2 minutes after the application, 5 ppm after 3 minutes, 1 ppm after 5 minutes, and 0.2 ppm after 10 minutes. During the in-transit fumigation, no phosphine was detected in the living and working areas of the ship. During unloading of the grain, the phosphine was detected downwind and at the edge of the hatch for 15 minutes. The concentration of phosphine was 4 ppm when the hatch was initially opened for aeration and dropped to 3 ppm after 5 minutes, 0.1 ppm after 10 minutes, and was non-detectable after 15 minutes. Phosphine was not detected at all of the other locations tested on the deck and the living and working areas of the ship. The application rate used in the study was 0.05 mg/cubic foot. If the maximum product label application rate (i.e., 0.145 gram/cubic foot), were used and the air concentrations increased proportionally, then during application the highest air concentration measured would increase from 7 ppm to 20.3 ppm. The highest phosphine concentration measured during aeration was 4 ppm. Normalizing this air concentration to the maximum application rate generates 11.6 ppm. The non-detects of the study can't be adjusted to the maximum application rate. However, they would be less than the lowest measured value of the study adjusted to the maximum application rate (i.e., 0.3 ppm) (Redlinger L.M., 1979).

The third study is described in another journal article on phosphine air concentrations generated on board a ship containing fumigated wheat. The wheat was loaded in to seven tanks on an oil tanker and was fumigated using aluminum phosphide tablets. The fumigant was applied via broadcasting the tablets onto the grain and then probing them into the grain. During application, air samples were taken downwind of the hatches on deck. The phosphine concentrations measured were reported as being below 0.3 ppm. During aeration of the holds, measurements were taken 10 meters downwind of the hatch within the first 5 minutes of aeration. Up to 5 ppm was detected. This air concentration decreased to non-detectable levels after 30 minutes. No phosphine was detected at any time in the living and working areas of the tanker. The application rate used in the study was 0.03 mg/cubic foot. If the product label application rate (i.e., 0.145 gram/cubic foot), were used and the air concentrations increased proportionally, then during aeration of the holds the highest air concentration measured would increase from 5 ppm to 24.2 ppm. The non-detects of the study can't be adjusted to the maximum application rate. However, they would be less than the lowest measured value of the study adjusted to the maximum application rate (i.e., 0.5 ppm) (Redlinger L.M., 1982).

The fourth study is described in a journal article on in-transit phosphine fumigation of corn on a bulk-dry cargo ship. The corn in three of the ship's holds was fumigated using aluminum phosphide tablets applied via the probe method where the fumigant is pushed underneath the surface of the grain using a pipe. During the application, samples were taken upwind and downwind of the hatches. There was no phosphine detected near the hatch of the first hold and 0.5 ppm of phosphine was detected downwind of the hatch for the second hold. However, less than 0.1 ppm phosphine was detected 2 minutes later. Less than 0.1 ppm phosphine was detected downwind of the hatch for the third hold during fumigation. During the in-transit fumigation, leakage of fumigant into the keel duct entrance to the engine room and the bow lockers occurred, generating phosphine air concentrations of 0.5 and 0.1 ppm, respectively. No results were reported for the living spaces of the ship. During aeration of the grain, when the hatches to the ship holds were opened, as much as 10 ppm was detected at the downwind and upwind sides of the edge of the hatch. The air concentrations decreased after 3 to 5 minutes to non-detectable levels. Phosphine on the surface of the grain where the workers were located was rarely detected. However, an air concentration of 0.3 ppm was measured in the free space above the grain in one of the holds when the workers arrived. After 15 minutes, however, the gas had dissipated. The application rate used in the study was 0.03 grams/cubic foot. If the maximum product label application rate (i.e., 0.145 gram/cubic foot), was used and the air concentrations increased proportionally, then during application the peak

measured value of 0.5 ppm would increase to 2.4 ppm. At the product label maximum application rate, the air concentrations measured in the engine room and bow lockers would increase to 2.4 and 0.5 ppm, respectively. Also the peak measured concentration of 10 ppm taken during aeration would increase to 48 ppm (Gillenwater H.B., 1981).
The fifth of the ship hold air monitoring studies is another investigation of in-transit fumigation of corn on a tanker. In the study, the corn in four of the ship's holds was fumigated using aluminum phosphide tablets while corn in another four holds was fumigated using bag blankets. During application samples were taken upwind and downwind of the hatches. Phosphine was detected on three occasions. Two of the cases were caused by a bag blanket that was left on the deck by the applicators. These instances generated air concentrations of 0.6 ppm. The third instance (0.5 ppm) was caused by a loose hatch cover which allowed fumes to escape the fumigated hold. The author reported that three instances were quickly rectified, immediately reducing the phosphine levels to undetectable levels within a few minutes. During in-transit fumigation, no phosphine was detected in the living spaces of the ship. However, a crack in the bulkhead generated 4 ppm of phosphine in a bosun's locker. The crack was inaccessible so the crew left the door to the locker room open, which dropped the phosphine air concentration to less than 0.1 ppm within 15 min. At the port of destination, the hatches to the holds containing fumigated grain were opened for aeration. Upon opening, downwind of the open hatches the phosphine levels ranged from undetectable to 0.5 ppm. The time required for the phosphine to reach undetectable levels varied between holds and ranged from 3 to 90 minutes. The application rate used in the study was 0.03 gram of phosphine/cubic foot. If the maximum product label application rate (i.e., 0.145 gram/cubic foot), were used and the air concentrations increased proportionally, then the peak measured value of 0.6 ppm measured downwind of the bag blanket on the deck during application would increase to 2.4 ppm. At the product label maximum application rate, the air concentration measured in the bosun's locker would have increased from 4 to 19 ppm. Also the peak measured concentration of 0.5 ppm taken during aeration would have increased to 2.4 ppm (Zettler J.L., 1982).

As mentioned previously, no TWA personal breathing-zone samples were taken. As a result, exposure estimates for the fumigant applicator, aerator, and occupational bystander scenarios were generated using a combination of ship hold information and surrogate data.

Applicator

The exposure estimates generated for the flat storage facility fumigant applicator were chosen to act as surrogate estimates for the handler applying fumigant to grain within the ship hold. Both the ship hold and flat storage facility are designed to house grain. Moreover, in the previously described references, the reported volumes of the ship holds ranged from 26,313 to 392,582 cubic feet. This range of volumes is similar to that for the flat storage facility which ranged from 112,500 to 587,500 cubic feet as reported in the previously described registrant task force study. Also, both types of structure were fumigated using the probe method for the tablet formulation and via the use of bag blankets. In addition, in the studies, the applicator had to enter the ship hold or flat storage facility to apply the fumigant to the grain, exit the structure, and then seal the exit. Hence, the short-term, seasonal, and annual exposure estimates for the ship hold applicator were assumed to be the same those for the flat storage facility applicator (Table 20).

Table 20. Commodity Fumigation and Aeration in Ships Holds: Exposure Estimates for the Applicator, Aerator, and Occupational Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.005	0.11	0.07
aerator [f]	0.08	0.02	0.01
occupational bystander (application) [g]	0.007	0.1	0.07
occupational bystander (aeration) [h]	0.009	0.2	0.13
occupational bystander (in-transit fumigation) [i]	0.1	0.1	0.07

[a] Due to a lack of data, the exposure estimates generated for fumigation and aeration of commodities in ship holds were chosen to act as surrogate estimates for commodity fumigation and aeration in ship holds using cylinderized phosphine gas and granular formulations.
[b] Short-Term Exposure: The applicator, occupational bystander (application), and occupational bystander (aeration) are assumed to be exposed to this estimated phosphine air concentration for 8 hr TWA/day. The occupational bystander (in-transit fumigation) on board the vessel during in-transit fumigation is assumed to be exposed to this estimated phosphine air concentration for 24-hr TWA/day. For short-term exposure, these daily exposures may last up to one week.
[c] Seasonal Exposure: The applicator, occupational bystander (application), and occupational bystander (aeration) are assumed to be exposed to this estimated phosphine air concentration for 8 hr TWA/day. The occupational bystander (in-transit fumigation) on board the vessel during in-transit fumigation is assumed to be exposed to this estimated phosphine air concentration for 24-hr TWA/day. The estimated use season is 8 months.
[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)
[e] The applicator entered the ship hold and layered the fumigant during the addition of grain to the hold or broadcasted and probed the fumigant into the loaded grain. No TWA breathing-zone data were available, hence, the flat storage facility applicator exposure estimates were used as surrogate estimates.
[f] The aerator opened the hatch to the hold containing fumigated grain after the ship arrived at the port of destination for unloading the grain. No TWA breathing-zone data were available, hence, the bulk car aerator exposure estimates were used as surrogate estimates.
[g] The occupational bystander (application) is assumed to work on deck near the ship hold hatches during fumigant application. No TWA breathing-zone data were available, hence, the bulk car post-application "nearby worker" exposure estimates were used as surrogate estimates.
[h] The occupational bystander (aeration) is assumed to work on deck near the ship hold hatches during aeration of the commodity. No TWA breathing-zone data were available, hence, the bulk car post-aeration "nearby worker" exposure estimates were chosen to act as surrogate estimates.
[i] The occupational bystander (in-transit fumigation) scenario is meant to represent the ship's crew during in-transit fumigation of the commodity in the hold. No TWA data were available; hence, the 24-hr TWA equivalent of the product label PEL restriction of 0.3 ppm was used to generate the exposure estimates.

Aerator

The exposure estimates for the bulk car aerator were chosen to act as surrogate estimates for the ship hold aerator. Although the bulk car, with volumes reported as ranging from

4100 to 4600 cubic feet, is substantially smaller than the ship hold, it is a better model than the other structures which were aerated in the registrant study, the warehouse and the box car. The warehouse is much larger than the bulk car but is less airtight. Moreover, the method of aeration differs from that of the ship hold. The box car with a reported volume ranging from 4500 - 6000 cubic feet is substantially smaller than the ship hold. In addition, the box car is opened via a sliding door on the side of the car. In contrast, the bulk car is aerated via hatches on top of the car much like the ship hold. Hence, the short-term, seasonal, and annual exposure estimates for the ship hold aerator were assumed to be the same those for the bulk car aerator (Table 20).

Occupational Bystander Exposure during Application and Aeration

Due to a lack of TWA breathing-zone data, the exposure estimates for the bulk car “nearby worker” post-application and post-aeration were chosen to act as surrogate estimates for the occupational bystander on deck during ship hold commodity fumigation and aeration, respectively (Table 20).

Occupational Bystander Exposure during In-Transit Fumigation

During in-transit fumigation of commodity in the ship hold(s), the crew could potentially be exposed while working within the ship. The crew would be on the ship 24 hours per day for potentially several weeks depending on the length of the voyage. No TWA breathing-zone samples were acquired in the previously described studies. However, as mentioned earlier, phosphine leakage from the holds containing fumigated grain occurred in-transit in two cases (Gillenwater H.B., 1981, and Zettler J.L., 1982). Also, the product labels state that no crew member is to be exposed to phosphine levels above the 0.3 ppm TWA PEL. Hence, the 24-hr TWA equivalent phosphine air concentration of 0.1 ppm was used to estimate exposure to the ship’s crew.

<u>Short-Term Exposure Estimate</u>
As stated earlier, the crew members are assumed to work and reside adjacent to the ship hold containing fumigated grain. Therefore, the bystander is anticipated to be exposed to a 24-hr TWA breathing-zone phosphine air concentration of 0.1 ppm (Table 20).

<u>Seasonal Exposure Estimate</u>
The estimated fumigant use season for the ship hold is 8 months. The occupational bystander adjacent to the ship hold is assumed to be exposed to a phosphine air concentration of 0.1 ppm 24-hr TWA for 8 months per year (Table 20).

<u>Annual Exposure Estimate</u>
Amortizing the seasonal exposure over the entire year, the occupational bystander is estimated to be exposed to 0.08 ppm PH_3 (24-hr TWA) throughout the year (Table 20).

Containers on Ships

Applicator and Aerator

In addition to ship hold fumigation, in-transit fumigation, according the product labels, may also be done using transport units (containers). No data were available for this use.

As a result, exposure estimates generated for the box car were utilized as surrogate estimates for fumigation and aeration of commodities in shipping containers on the ship. Of the available surrogate data, box cars, due to their shape, size, and large doors, most closely resemble shipping containers. Assuming the shipping container is stored on the deck of the ship, the box car fumigation and outdoor aeration exposure estimates were used as surrogates for the container fumigant application and aeration scenarios (Table 21).

Occupational Bystander Exposure during Application and Aeration

Occupational bystanders adjacent to the shipping container could potentially be exposed to phosphine during fumigant application and commodity aeration. However, no exposure data was generated for these scenarios. As a result, the exposure estimates generated for the box car "nearby worker" during application were chosen to be used as surrogate estimates for the occupational bystander on the deck of the ship working near a shipping container undergoing commodity fumigant application. The exposure estimate generated for the "nearby worker" for bulk car post-aeration was chosen to act as a surrogate exposure estimate for shipping container commodity aeration. A box car "nearby worker" post-aeration exposure estimate was generated also. However, this scenario was assumed to occur indoors in an area with poor ventilation. In contrast, the shipping container was assumed to be located on the deck of the vessel where ventilation would be relatively high. Hence, the bulk car post-aeration "nearby worker" exposure estimates for commodity aeration were selected to be used as surrogate estimates for the occupational bystander nearby an aerating shipping container. As discussed earlier, the exposure data suggests that the bulk car aeration took place in a well-ventilated area (Table 21).

Occupational Bystander Exposure during In-Transit Fumigation

Due to a lack of data, the residential bystander exposure estimates generated for the box car fumigation were chosen to be utilized as surrogate estimates for occupational bystander exposure during in-transit fumigation of shipping containers (Table 21).

Table 21. Commodity Fumigation and Aeration in Containers on Ships: Exposure Estimates for the Applicator, Aerator, and Occupational Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.08	0.01	0.007
aerator [f]	0.06	0.02	0.013
occupational bystander (application) [g]	0.03	0.3	0.2
occupational bystander (aeration) [h]	0.009	0.2	0.13
occupational bystander (in-transit fumigation) [i]	0.1	0.1	0.07

[a] Due to a lack of data, the exposure estimates generated for fumigation and aeration of commodities in containers on ships were chosen to act as surrogate estimates for commodity fumigation and aeration in containers on ships using cylinderized phosphine gas and granular formulations.

[b] Short-Term Exposure: The applicator, occupational bystander (application), and occupational bystander (aeration) are assumed to be exposed to this estimated phosphine air concentration for 8 hr TWA/day. The occupational bystander (in-transit fumigation) on board the vessel during in-transit fumigation is assumed to be exposed to this estimated phosphine air concentration for 24-hr TWA/day. For short-term exposure, these daily exposures may last up to one week.

[c] Seasonal Exposure: The applicator, occupational bystander (application), and occupational bystander (aeration) are assumed to be exposed to this estimated phosphine air concentration for 8 hr TWA/day. The occupational bystander (in-transit fumigation) on board the vessel during in-transit fumigation is assumed to be exposed to this estimated phosphine air concentration for 24-hr TWA/day. The estimated use season is 8 months.

[d] Annual Exposure: seasonal exposure air concentration x (8 months of seasonal exposure/12 months in a year)

[e] The applicator entered the ship hold and layered the fumigant during the addition of grain to the hold or broadcasted and probed the fumigant into the loaded grain. No TWA breathing-zone data were available, hence, the box car applicator exposure estimates were selected to act as surrogate estimates.

[f] No TWA breathing-zone data were available, hence, the box car outdoor aerator exposure estimates were chosen to be used as surrogate estimates.

[g] The occupational bystander (application) is assumed to work on deck near the ship hold hatches during fumigant application. No TWA breathing-zone data were available, hence, the box car “nearby worker” occupational bystander exposure estimates generated for exposure during fumigant application were chosen to act as surrogate estimates.

[h] The occupational bystander (aeration) is assumed to work on deck near the shipping containers during aeration of the commodity. No TWA breathing-zone data were available, hence, the bulk car post-aeration “nearby worker” occupational bystander exposure estimates were chosen to act as surrogate estimates.

[i] The occupational bystander (in-transit fumigation) scenario is meant to represent the ship’s crew during in-transit fumigation of the commodity in the shipping container. No TWA data were available, hence, the 24-hr TWA equivalent of the product label PEL restriction of 0.3 ppm was used to generate the exposure estimates.

Spot Fumigation

The data used to estimate exposure was obtained from the same registrant task force study used to estimate exposure for the workers fumigating/aerating farm bins and flat storage facilities, warehouses, and rail cars. In the study, spot fumigation and aeration of equipment and specific areas within a flour and corn mill were conducted. The mills had multiple stories and the mill equipment fumigated consisted of grain processing equipment such as cyclones, sifters, bins, purifiers, hoppers, dusters, and roll stands. In addition, grain transporting equipment, such as elevator legs, boots, and augers, was also fumigated.

The steps for spot fumigation within the two mills are preparation of the structure, application of the fumigant, aeration of the structure, and retrieval of the spent fumigant strips. The preparation step consisted of sealing the vents on the roofs of the two mills and marking areas and equipment within the mills for fumigation using cloth ribbons. Metal clips attached to the ends of the cloth strips were used for holding the fumigant which consisted of strips of gas-permeable fleece containing pellets of magnesium phosphide. Following the preparation step, the workers entered each warehouse and, working from the top floor down, attached the fumigant strips to each cloth ribbon. The amount of fumigant (i.e., number of pellets), was determined by the size of the piece of equipment. During the application step, plastic bags were left in a conspicuous location on each floor for later retrieval of the fumigant. After the application of fumigant, the workers exited the mills on the ground level and sealed and placarded all of the entrances. Four workers conducted the application which took 33 minutes for the two mills. The mean breathing-zone sampling period was 67 minutes [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The product label for this formulation provides general guidelines for spot treatment of various types of equipment within mills. The procedures followed in the exposure study are similar to these product label guidelines.

After about 36 hours, the workers returned to aerate the mills and retrieve the spent fumigant strips. Prior to entering each floor, the phosphine air concentration was measured using a length-of-stain dosimeter or electrochemical detector. Once the air concentration measured below 0.3 ppm, the workers entered the floor opened the windows and outside doors. The plastic sheeting was removed from the roof vents and the fans were turned on. If phosphine air concentrations were found to be greater than 0.3 ppm, the crew opened additional windows and doors [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

After the mills aerated for 15 minutes the workers started to retrieve the spent fumigant. The crew started on the top floor of the building and retrieved the spent fumigant on each floor. Respiratory protection was not used during retrieval since the phosphine levels were “generally well below 0.3 ppm”. After exiting the building, the spent fumigant strips were submerged and deactivated in a 55-gallon drum filled with water. The aeration, strip retrieval, and deactivation were conducted by three workers. The mean sampling time was 93 minutes [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

In total, 4 replicates were generated in the registrant study for the applicator, and 3 replicates for the aerator/retriever/deactivator. The mean breathing-zone air concentration for the 4 applicators is 3.1 ppm while that for the aerator/retriever/deactivator is 0.06

ppm. If the phosphine air concentrations are corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study, then the mean phosphine air concentrations for the applicator and aerator/retriever/deactivator increase to 36.6 ppm and 0.75 ppm, respectively. The highest work shift breathing-zone air concentrations, corrected for recovery if < 90%, multiplied by the product label maximum application rate, and divided by the application rate used in the exposure study are 41.6 ppm and 0.8 ppm for the applicator and aerator/retriever/deactivator, respectively. The product label maximum application rate is 10 times higher than the application rate used in the exposure study.

Short-term exposures for the applicator conducting spot fumigation or aeration/retrieval/deactivation were estimated using the highest work shift breathing-zone air concentration. Even though the fumigation step only took 33 minutes, due to a lack of data, the applicators, in a worst-case scenario are assumed to be exposed to an 8-hr TWA phosphine air concentration of 41.6 ppm. As mentioned in the PUR section, according to the PUR database, relatively low levels of fumigant were used in California during 2006-2010 for spot fumigation. As a result only short-term exposure was estimated for this use.

According to the product labels, in addition to the strips of gas-permeable fleece containing pellets of magnesium phosphide used in the exposure studies, spot fumigation can also be conducted using aluminum phosphide tablets or pellets, magnesium phosphide tablets, polyethylene plates impregnated with magnesium phosphide, or, potentially, via a phosphine generator, granules containing aluminum phosphide or magnesium phosphide. Spot fumigation might also be conducted using cylinderized phosphine gas. Due to a lack of data, the exposure estimates generated for spot fumigation using strips of gas-permeable fleece containing pellets of magnesium phosphide were chosen to act as surrogate estimates for these other formulations.

Due to a lack of data, the estimates generated for spot fumigation sites were chosen to act as surrogate estimates for the beehive, and small sealable enclosure which are listed on some of the product labels.

Applicator

Short-Term Exposure Estimate

Short-term exposure is defined as acute exposure and exposures up to a week in duration. The handler wearing respiratory protection, in this case a SCBA, while conducting spot fumigation is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.004 ppm (Table 22).

Aerator/Retriever/Deactivator

Short-Term Exposure Estimate

The handler wearing an NIOSH/MSHA approved full-face gas mask-phosphine canister combination while conducting aeration/retrieval/deactivation is anticipated to be exposed to an 8-hr TWA phosphine air concentration of 0.02 ppm (Table 22).

Occupational Bystander

No useable data was available for estimating the 8-hr TWA exposure to the occupational bystander working adjacent to the structure undergoing spot fumigation or aeration. However, as mentioned earlier, air concentration data for fumigating and aerating structures suggest that the 0.3 ppm PEL could be exceeded [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022]. As a result, the assumed short-term exposure estimate for the occupational bystander working adjacent to a structure undergoing spot fumigation or aeration is the legal maximum allowable exposure of 0.3 ppm (8-hr TWA) as stated on the product labels.

Short-Term Exposure Estimate

The occupational bystander working adjacent to the structure during spot fumigation or aeration is anticipated to be exposed to a phosphine air concentration of 0.3 ppm (8-hr TWA) (Table 22).

Residential Bystander

The residential bystander is assumed to reside adjacent to the structure undergoing spot fumigation or aeration. The data available to estimate potential phosphine exposure during fumigation and aeration is that previously described in the occupational bystander exposure section. Since the residential bystander is assumed to reside adjacent to the structure, the 24-hr TWA equivalent of the PEL (i.e. 0.1 ppm) was used to estimate the short-term exposure estimate (Table 22).

Table 22. Spot Fumigation:
Exposure Estimates for the Applicator, Aerator/Retriever/Deactivator, Occupational Bystander, and Residential Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator [e]	0.004	n/a	n/a
aerator/retriever/deactivator [f]	0.02	n/a	n/a
occupational bystander [g]	0.3	n/a	n/a
residential bystander [h]	0.1	n/a	n/a

[a] Except for the occupational and residential bystanders, the exposure estimates generated in this table are from breathing-zone air concentrations which have been corrected for recovery, if < 90%, and multiplied by the maximum product label application rate/application rate used in the exposure study. The exposure estimates generated in this table are from breathing-zone air concentrations which have been adjusted to the maximum application rate and corrected for recovery if the field-fortification study yielded a mean sample recovery < 90%. Except for the residential bystander, if an exposure estimate was > 0.3 ppm, then the estimate was reduced by the appropriate respiratory protection factor (i.e., 98% for the full-face respirator equipped with a canister and 99.99% for SCBA). Due to a lack of data, the estimates generated for spot fumigation were chosen to act as surrogate estimates for spot fumigation of the beehive, and small sealable enclosure which are listed on some of the product labels. In addition, these estimates were chosen to act as surrogate estimates for spot fumigation using cylinderized phosphine gas, or granular formulations.

[b] Short-Term Exposure: phosphine air concentration to which the applicator, aerator/retriever/deactivator, occupational bystander are exposed to for 8-hr TWA/day. The residential bystander is assumed to be exposed the estimated phosphine air concentration for 24-hr TWA/day. Short-term exposure is assumed to last for up to one week.

[c] Seasonal Exposure: n/a (not applicable). Based upon Pesticide Use Report data, minimal amounts of fumigant was used for spot fumigation in California from 2006-2010. Hence, no intermediate-term exposure estimates were generated.

[d] Annual Exposure: n/a (not applicable). Based upon Pesticide Use Report data, minimal amounts of fumigant was used for spot fumigation in California from 2006-2010. Hence, no intermediate-term exposure estimates were generated.

[e] The applicator sealed the mill for spot fumigation, marked equipment and specific locations within the structure for fumigation, and then applied the fumigant at the marked locations throughout the structure. Upon exiting the mill, the handler sealed and placarded all of the exits. The data set for this scenario consists of 4 replicates ranging in value from 32.1 to 41.6 ppm.

[f] The aerator/retriever/deactivator aerated the mill after the fumigation, retrieved the spent fumigant strips, and deactivated the residual fumigant outside of the mill in a barrel containing water. The data set for this scenario consists of 3 replicates ranging in value from 0.7 to 0.8 ppm.

[g] The occupational bystander is assumed to work adjacent to the structure undergoing spot fumigation for 8 hours per day and, due to a lack of exposure data, is assumed to be exposed to the product label 8-hr TWA PEL of 0.3 ppm.

[h] The residential bystander is assumed to reside adjacent to the structure undergoing spot fumigation for 24 hours per day and, due to a lack of exposure data, is assumed to be exposed to the 24-hr TWA equivalent of the 8-hr TWA PEL of 0.3 ppm.

Burrowing Pest Fumigation

Two studies were considered for estimating phosphine exposure to applicators and bystanders during burrow fumigation. The first study was obtained from a journal article whose author investigated inhalation exposure to phosphine and the deposition of aluminum phosphide dust on the clothing of workers applying fumigant tablets by hand or via the use of a tablet dispenser (Baker, 1992). One goal of the study was to determine which of two application methods (hand vs. dispenser) generates less exposure to the worker. Another goal of the study was to determine the rate of dissipation of aluminum phosphide on the gloves and clothing contaminated with fumigant dust. The methodology for the inhalation exposure study consisted of using colorimetric badges attached to the collar of the applicator to measure long term (i.e., 8-hr TWA) phosphine air concentrations in the breathing zone. Phosphine gas detector tubes were used to obtain instantaneous air samples from the breathing zone of the handler during application. The methodology used for measuring aluminum phosphide dust on the worker's clothing consisted of separately bagging the gloves, shirt, and pants of the handler after the application. The sealed 1.5 cubic foot bag was then opened and the air inside sampled immediately or 30 minutes to 2 hours after the sample was bagged.

The investigators reported that the instantaneous samples of the breathing-zone rarely contained phosphine. The only time phosphine was detected was when the handler opened the fumigant container close to the body or when filling the tablet dispenser. The PEL phosphine air concentration of 0.3 ppm was reached for a few seconds when a storage box, presumably containing fumigant was opened.

The TWA breathing-zone phosphine air concentrations detected in the study were predominantly reported as 0.0 ppm. Twenty-one air monitoring samples were generated over three days of monitoring 7 hand applicators per day. Of the 21 samples, only 4 samples were above 0.0 ppm. The samples were collected over 8-hr work shifts and the 8-hr TWA air concentrations were 0.1, 0.1, 0.05, and 0.012 ppm. For the "mechanical" application method where a tablet dispenser was used, no phosphine was detected over the 3 days of monitoring of 7 applicators per day. The inhalation data from the study was not used to estimate exposure. The colorimetric badges used to generated the TWA breathing-zone air concentrations were reported as being sensitive from 0.1 to 2.4 ppm, and, therefore, not quantitative at the phosphine levels detected in the study.

The clothing and gloves of the worker were shown to be contaminated with aluminum phosphide dust. The fumigant applicators were sampled from 2 to 4 work days. Eight workers applied the fumigant using a mechanical dispenser while 8 workers applied the tablets manually. No phosphine was detected in 64% of the shirt samples taken from the workers using the mechanical dispenser. Phosphine was not detected in 58% of the shirt samples taken from the manual applicators. The mean phosphine air concentration in the bags containing mechanical dispenser shirt samples is 0.07 ppm with the highest sample containing 0.3 ppm phosphine. The corresponding sample concentrations for the manual applicators are 0.29 and 4.9 ppm phosphine, respectively. Forty-four percent of the pant samples from the applicators using the mechanical dispenser had no detectable levels of phosphine. Nineteen percent of the samples from the manual applicators had no detectable levels of phosphine. The mean and high values for the pant samples from the applicators using the mechanical dispenser are 0.167 and 1.2 ppm, respectively. The corresponding values for the manual applicators are 0.875 and 12 ppm, respectively. Finally, phosphine was not detected in 24% of the glove samples from the applicators using the mechanical dispenser and 19% of the glove samples from the applicators manually applying the tablets. The mean and high values for the glove samples from the handlers using the mechanical dispenser are 0.59 and 6 ppm, respectively. The corresponding values for the manual applicators are 2.11 and 40 ppm, respectively.

The second study considered for estimating exposure is an investigation of phosphine exposure to certified applicators and non-certified applicators, under supervision, during application of aluminum phosphide tablets to rodent burrows. In addition, potential phosphine exposures to bystanders in buildings adjacent to the treated area or who enter the treated area were measured [Cytec Industries, Inc. (2004) Registration Package Number 51882-0022]. The application activities consisted of applying the maximum label rate of 4 tablets into each burrow entrance, stuffing paper into the hole, and filling in behind the paper wad with soil. This procedure is the same as that stated in the current product labels for the tablet formulations. Over 41,000 tablets of the aluminum phosphide fumigant (Pestcon Fumitoxin® ALP), were applied during the study by 12 certified applicators, and 21 non-certified applicators. The certified applicators were monitored while treating burrows in areas such as school ground parks, golf courses, residential yards, rights-of-way, and industrial parks. The non-certified applicators varied in levels of experience from those having training but no actual experience applying the fumigant to those who were experienced applicators. These applicators were monitored for phosphine exposure while treating burrows in almond, plum, prune, peach, and walnut orchards.

TWA breathing-zone phosphine levels were measured using colorimetric badges and gas detectors. The colorimetric badge was attached to the wearer in or near the breathing-zone (i.e., front shirt or vest pocket, suspended from a neck strap, or attached to the collar). The badges could detect phosphine levels ranging from 0.01 to 0.3 ppm over an 8-hr sampling period. The gas detectors were placed in the shirt pocket and were specified as having a reproducibility of ±0.02 ppm. These devices had a detection range of 0.01 to 20 ppm, and could sample the air in the breathing-zone regularly for the entire work shift. Depending on the portion of the study, the gas detectors sampled the air in 1-, 5-, or 15-minute intervals and recorded the measured air concentrations. Colorimetric detection tubes were used to verify phosphine readings from the gas detectors and to check for interfering gases. The data from the colorimetric badges were not used to estimate exposure due to false positives. Hence, exposure was estimated using the gas detector data.

To control for contaminating gasses which could produce false positive readings on the detectors, a background control study was conducted. This experiment was carried out prior to the aluminum phosphide application and consisted of monitoring the application sites for the "cross gasses" hydrogen sulfide and carbon monoxide. The contaminating gasses at the treatment sites were found to be "very low", ranging from 0.01 to 0.02 ppm.

Nine sites were treated with aluminum phosphide in the study. The sites varied in size from 1.5 to 40 acres. These sites consisted of turf and agricultural crops and were reported as being moderately to heavily populated with pocket gophers and ground squirrels. Two of the sites were reported as having "the heaviest ground squirrel infestations observed for many years by the Principal Investigator".

In addition to applicator exposure, the registrant measured exposure to the reentry worker, occupational bystander, and residential bystander. To characterize reentry worker exposure, at each of the aforementioned treated sites, the investigators attached gas detectors equipped with data loggers to stakes or trees adjacent to the treated site. Gas detectors were also placed 3.5 to 4 feet above ground in the middle of the most heavily treated area with detectors generally being located directly over treated burrows. Another gas detector was placed approximately one foot above ground, downwind of the treated site, and within 25 to 100 feet of the closest treated burrow. The occupational and residential bystander scenarios investigated in the study were for persons in buildings adjacent to the treatment site. For this part of the study, 29 structures were monitored. Twenty were houses which were adjacent to areas being treated for pocket gophers with ten of the houses having raised foundations and ten having slab foundations. For each house, two windows were opened by approximately 4 inches on each side during the study. The gas detectors were placed in areas of the structure which had the most air flow and in the bedroom closest to the treated field. Measurements were taken during the afternoon and evening when the wind blew from the treated field towards the house. The other 9 structures were adjacent to sites being treated for ground squirrels with five of the buildings with raised foundations and five with slab foundations. The 9 structures consisted of two offices with a large commons area, 3 apartments, one residence, one attached study, a storage shed, and a small residence of 510 square feet. The 510 square foot structure was monitored twice. However, the data from one of the studies was rejected due to improper application methods and the presence of another pesticide which may have produced a false-positive. The windows on these 9 structures were opened unless air was pulled into the building from the outside for ventilation. The gas detector was placed inside of each structure on the wall closest to the field being treated with fumigant. Each building was monitored for 1 to 2 days prior to the application of aluminum phosphide to characterize the background signal and then 2 to 3 days after the application to estimate bystander exposure. Aluminum phosphide applications to burrows were made at least 15 feet away from each structure.

The overall results indicate that the certified and non-certified applicators had phosphine exposure levels below the 8-hr TWA PEL of 0.3 ppm. The mean of the 8-hr TWA exposure measurements for the both the certified and non-certified applicator is 0.035 ppm. The highest 8-hr TWA exposure was 0.22 ppm. The certified applicators had a mean 8-hr TWA breathing-zone phosphine air concentration of 0.02 ppm while the non-certified applicators had a mean 8-hr TWA breathing-zone air concentration of 0.04 ppm. The highest individual TWA air concentration for a certified applicator was 0.12 ppm while that for a non-certified applicator was 0.22 ppm. The 15-min TWA STEL air concentration of 1 ppm on the product labels must not be exceeded and must not be reached more than 4 times/day. The 1 ppm air concentration was reached once by a certified applicator and a total of thirteen times by the non-certified applicators. However, no individual applicator exceeded 1 ppm more than twice/day. The study provides a graph of the recorded gas detector data for phosphine exposure to a non-certified worker which had a peak exposure of 6.9 ppm for approximately 5 minutes. The exposure was reported to be due to the use of poor technique while opening a container of fumigant. These data suggest that the 8-hr TWA exposures are likely the result of numerous episodic exposures of relatively high air concentrations of phosphine.

The amount of time spent applying fumigant during the work shift varied. Most of the applicators treated burrows throughout the 8-hr work shift. However, some of the applicators treated burrows for only 1 to 4 hours per day, spending the rest of the workday traveling or carrying out other duties. To compensate for this variable, the data was processed by the registrant using the "Gas Vision 4.0" data program to calculate average TWA breathing-zone air concentrations for just the period spent applying fumigant. For estimating exposure, these processed data were assumed to be 8-hr TWA air concentrations for the certified and non-certified applicators applying fumigant for the entire 8-hr workday. The highest individual measured TWA air concentrations for these processed data were 0.22 ppm and 0.24 ppm. These values were used to estimate short-term exposure for the certified and non-certified applicators, respectively. For estimating seasonal and annual exposures, the means of the processed data, 0.03 ppm and 0.06 ppm, were used to estimate intermediate exposure estimates for the certified and non-certified applicators, respectively.

Certified Applicator

Short-Term Exposure Estimate

Short-term exposure is defined as acute exposure and exposures up to one week in duration. The estimated work shift breathing-zone air concentration of the certified applicator is 0.22 ppm (8-hr TWA) (Table 23).

Table 23. Burrowing Pest Fumigation: Exposure Estimates for the Applicator, Reentry Worker, and Occupational Bystander [a]

Exposure Scenario	Short-Term Exposure (ppm) [b]	Seasonal Exposure (ppm) [c]	Annual Exposure (ppm) [d]
applicator (certified) [e]	0.22	0.03	0.01
applicator (non-certified) [e]	0.24	0.06	0.03
reentry worker [f]	0.06	n/a	n/a
occupational bystander in structure located 100 feet away from treated field [g]	0.03	n/a	n/a

[a] The exposure study was conducted using aluminum phosphide. The exposure estimates were generated assuming that the worker was not wearing PPE. Due to a lack of data, the exposure estimates were chosen to act as surrogate estimates for burrowing pest fumigation conducted with magnesium phosphide.

[b] Short-Term Exposure: The applicator, occupational bystander (application), and occupational bystander (aeration) are assumed to be exposed to this estimated phosphine air concentration for 8 hr TWA/day. For short-term exposure, these daily exposures may last up to one week.

[c] Seasonal Exposure: phosphine air concentration to which applicator is exposed to for 8-hr TWA for a season of 6 months. For the reentry worker, reentry bystander, and occupational bystander, intermediate-term exposure estimates were not generated since this type of exposure is unlikely.

[d] Annual Exposure: seasonal exposure air concentration amortized over entire year

[e] The certified and non-certified applicators added aluminum phosphide tablets to the maximum application rate of 4 tablets per burrow system. For the certified applicator the exposure estimates were generated using 38 replicates which ranged from none detected to 0.22. For the non-certified applicator, the exposure estimates were generated using 70 replicates which ranged from none detected to 0.24.

[f] The reentry worker scenario represents the worker entering the treated field post-application. Daily exposure throughout the season is unlikely. Hence, only short-term exposure was estimated. The exposure estimate was generated using a total of 9 sites which were monitored for 8 hours/day using 3 air samplers/field. A total of eight 8-hr TWA sample air concentrations for 8 sites were reported for the pre-application or control days. No phosphine was detected in the control samples. A total of twenty-six 8-hr TWA sample air concentrations at all 9 sites were reported for up to 3 days post-application. Twenty of these reported air concentrations had no detectable levels of phosphine while 6 of these air concentrations ranged from 0.01 to 0.06 ppm.

[g] Based on the permit conditions issued by DPR, the occupational bystander is assumed to work in a structure located 100 feet away from the edge of the treated field. Only the short-term exposure estimate of 8 hours TWA was used to estimate exposure since exposure throughout the season is unlikely. A total of thirty-two 8-hr TWA air concentrations were reported for a total of 61 structures. The reported results were consolidated based upon the type of foundation (i.e., raised or slab) of the structure and the structure’s location. Due to a lack of data, the 8-hr TWA phosphine air concentration measured 15 feet from the treated field was used as a surrogate exposure estimate for the occupational bystander in a structure located 100 feet from the treated field.

Seasonal Exposure Estimate

During 2006-2010, the bulk of burrowing pest fumigations was conducted using aluminum phosphide. The use season for this fumigant during 2006-10 is 6 months. Hence, the certified applicator is anticipated to be exposed to a phosphine air concentration of 0.03 ppm (8 hr TWA) each day for 6 months of the year (Table 23).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the certified applicator is anticipated to be exposed to 0.01 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 23).

Non-certified Applicator

Short-Term Exposure Estimate

Short-term exposure is defined as acute exposure and exposures up to week in duration. The estimated work shift breathing-zone air concentration of the non-certified applicator is 0.24 ppm (8 hr TWA) (Table 23).

Seasonal Exposure Estimate

During 2006-2010, the bulk of burrowing pest fumigations was conducted using aluminum phosphide. The use season for this fumigant during 2006-10 is 6 months. Hence, the non-certified applicator is anticipated to be exposed to a phosphine air concentration of 0.06 ppm (8 hr TWA) each day for 6 months of the year (Table 23).

Annual Exposure Estimate

Amortizing the seasonal exposure over the entire year, the non-certified applicator is anticipated to be exposed to 0.03 ppm PH_3 (8 hr TWA) each day over the course of the year (Table 23).

The 8-hr TWA air concentrations obtained in the reentry worker and bystander studies were below the 0.3 ppm 8-hr TWA PEL. For the reentry worker scenario concerning persons entering a treated field, a total of 9 monitoring experiments were conducted on three different types of sites. The first type consisted of 3 irrigated turf sites being treated for pocket gophers. These sites ranged in size from 1.5 to 10 acres and were designed to simulate parks and school grounds. The control study measurements, done prior to the application, and the treatment study measurements, done for 3 days post application, showed no levels high enough to generate an 8-hr TWA. The highest instantaneous levels measured ranged from 0.02 to 0.32 ppm. In total, twelve 8-hr TWA phosphine air concentrations were reported for the 3 sites. Four air concentrations were listed for each site with one value for the control pre-application day and 1 value for each of the 3 post-application days.

The second type of site consisted of 3 orchards being treated for ground squirrels. These plots ranged in size from 8 to 20 acres. The pest populations were considered to be moderate to heavy. At two of the sites, phosphine concentrations were too low to generate an 8-hr TWA air concentration for both the control studies and the post application studies. However, the third site was heavily infested with ground squirrels, requiring more aluminum phosphide tablets, and had an 8-hr TWA air concentration of 0.05 ppm on the first night post application and 0.02 ppm on the second night post application. Data for the pre-application control period and the third day post-application were not available. In total, ten 8-hr TWA air concentrations were generated for the 3 sites. The first site had one air concentration generated for the pre-application day and 1 concentration for each of the 3 post-application days. This was also the case for the second site. However, as mentioned earlier, the third site lacked results for the pre-application day and the third post-application day.

The third type of site consisted of 3 areas, ranging in size from 2.5 to 20 acres, treated for both pocket gophers and ground squirrels. One of the sites had phosphine concentrations which were too low to generate an 8-hr TWA air concentration on the pre application control day and for all three of the post application days. Another site also had levels too low to generate an 8-hr TWA except for the third day post application. Finally, the third treatment site, heavily infested, had phosphine air concentrations which were too low to generate an 8-hr TWA air concentration on the pre application control day but had 8-hr TWA air concentrations of 0.01, 0.06, and 0.03 ppm on the first, second, and third nights post application, respectively. Of all the 8-hr TWA air concentrations generated in the study, the highest single 8-hr TWA air concentration reported (i.e., 0.06 ppm), was utilized to estimate short-term exposure to the worker entering a treated field. The product label maximum application rate of 4 tablets per hole was used in the study. Since it is unlikely that the reentry worker would enter or work alongside a treated field every day of the use season or year, only the short-term estimate was generated. In total, twelve 8-hr TWA air concentrations were reported for the 3 sites. Four 8-hr TWA air concentrations were reported for each site with one 8-hr TWA air concentration for the control pre-application day and one 8-hr TWA air concentration for each of the 3 post-application days.

Reentry Worker

The short-term exposure estimate for the individual entering a treated field is 0.06 ppm (8-hr TWA) (Table 23).

The bystander study for persons occupying buildings adjacent to the treated sites generated 8-hr TWA air concentrations which were below the 0.3 ppm 8-hr TWA PEL. Of the 20 residences adjacent to (i.e., yard of house), pocket gopher treatment sites, that were monitored for up to 72 hours post application, only two of the houses had phosphine air concentrations high enough to generate 8-hr TWA air concentrations. One of the structures had a raised foundation and had 8-hr TWA air concentrations of 0.03 ppm on the first night after the application and 0.01 ppm on the second night. The second house had a slab foundation and an 8-hr TWA air concentration of 0.02 ppm on the first night post application. A total of three (1 per each of three post-application days) 8-hr TWA air concentrations were reported for the 10 units with raised foundations and two 8-hr TWA air concentrations for the first two post-application days for the ten structures with slab foundations. The reported air concentrations were consolidated based upon the type of foundation and the location of the site.

For the ten buildings near (i.e., 15 to 200 feet away), treated ground squirrel plots, no 8-hr TWA air concentrations could be detected within any of the structures. Background air monitoring was reported to have been conducted at each site prior to the application. The data was not listed. However, the author stated that "if phosphine was detected during the control period, it was commonly traceable to empty sewer traps or uncovered sewer clean-out caps. All sink and bathroom drain traps were filled with water to block entry of the gases prior to the last control day to further insulate the site". For this study, fourteen 8-hr TWA air concentration data were reported. The samples were taken for each of three days post-application in 6 of the structures, and each of 2 days post-application in the other 4 structures. The reported air concentrations were consolidated based upon the type of foundation and the location of the site.

The author states in the results section that prior to the acceptance of the protocol for the aforementioned monitoring experiments, a pilot study was carried out at a separate site containing 18 houses with raised foundations and 13 houses with slab foundations. These structures were supposedly adjacent to fields being fumigated with aluminum phosphide to control ground squirrels. This study was reported as having no phosphine air concentrations high enough to generate 8-hr TWA phosphine air concentrations.

For estimating exposure, the aforementioned highest 8-hr TWA air concentration of the study (i.e., 0.03 ppm), was used to calculate short-term exposure for the bystander in a structure located 100 feet away from a treated field. This air concentration was obtained in the portion of the study containing monitoring data for houses with the yards being treated for gophers. The author stated that a 15-foot buffer was used for application. Recent permit conditions issued by DPR to the county agricultural commissioners require that a buffer zone of 100 feet must exist between the fumigated burrow opening(s) and a structure potentially occupied by humans and/or domestic animals (DPR, 2012b). This increased buffer-zone was implemented by EPA. As stated by the enforcement branch of DPR, "In 2010, the U.S. EPA required additional use restrictions, including a 100 foot distance from structures, in response to two deaths in Utah." (DPR, 2012c). Due to a lack of data, the phosphine air concentration measured at 15 feet from the treated field was used as a surrogate air concentration for phosphine at 100 feet from the treated field. Hence, the 8-hr TWA short-term exposure estimate for the occupational bystander in a structure located 100 feet away from the treated field is 0.03 ppm. The occupational bystander is unlikely to work in a building near a treated field throughout the use season. Hence, only the short-term exposure estimate was generated.

Occupational Bystander in Structure Located 100 feet from the Edge of a Treated Field

The estimated work shift breathing-zone air concentration of the occupational bystander in a structure located 100 feet away from the treated field is 0.03 ppm (8-hr TWA) (Table 23).

Residential Bystander

Recent permit conditions issued by DPR to the county agricultural commissioners contain the following requirements: "Use of aluminum and magnesium phosphide is strictly prohibited around all residential areas, including single and multi-family residential properties, nursing homes, schools (except athletic fields, where use may continue), day care facilities, and hospitals." (DPR, 2012b). As a result, residential bystander exposure to phosphine due to burrowing pest treatment is not anticipated.

Ambient Exposure Away From Applications

The California Air Resources Board (CARB), pursuant to the provisions of AB 1807 and AB 2728, identifies phosphine as being a toxic air contaminant. Per DPR policy, in addition to estimating bystander exposure for individuals located within or near the facility or field being treated, exposure to ambient phosphine due to fumigant application was also assessed. As stated earlier, no useable monitoring data for phosphine in ambient air (away from applications) in California are available from CARB. Moreover, phosphine is not included in the list of pesticidal active ingredients monitored by DPR in its Air Monitoring Network, which is only able to monitor a finite set of chemicals. A total of 34 chemicals included in the Air Monitoring Network list were prioritized based on criteria that included high use, volatility, high priority for risk assessment, and the feasibility of inclusion in a multi-residue monitoring method. Phosphine did not meet the last criterion. Because phosphine is listed as a Toxic Air Contaminant, DPR requested ambient air monitoring be conducted by the California Air Resources Board in a high-use area during a time when use was anticipated to be high. Exposures to phosphine in ambient air are anticipated to be equal to or less than bystander exposures, as the highest pesticide concentrations in air occur adjacent to an application. Bystander exposure estimates are thus health-protective estimates for airborne phosphine exposures both adjacent to and away from applications. Non-pesticidal sources of phosphine which may contribute to ambient exposure are sewage treatment plants, marshes, landfills, or rice paddies may generate higher levels than fumigation (Han S., 2000).

EXPOSURE APPRAISAL

General Assumptions

The assumptions made in this EAD may have led to under- or overestimation of exposure. The first assumption is that the handler and occupational bystander are located in the highest use county for the entire season. This assumption, however, may be incorrect, leading to overestimation of exposure. Another assumption which creates uncertainty is that the TWA phosphine air concentrations measured for periods of less than 8, 9.7, or 12 hours, depending upon the particular scenario, are equal to the respective 8-, 9.7-, or 12-hr TWA air concentration. In some cases, the sampling times were well under an hour. Using this assumption may lead to under- or overestimation of exposure. However, due to a lack of data and the anticipated work periods used for estimating exposure, this assumption was made.

In scenarios where the handler and bystander were in potentially closed environments and level of ventilation was unknown, the worker was assumed to use PPE instead of engineering controls to reduce breathing-zone phosphine levels. The product labels contain a section for “Engineering Controls and Work Practices”, which has language instructing the worker to “use engineering controls and/or appropriate work practices” to “reduce exposure to within permitted limits”. An “appropriate work practice” could be wearing proper PPE. Hence, the worker was assumed to don PPE instead of using engineering controls to reduce the breathing-zone phosphine air concentrations. This assumption may be incorrect. Moreover, if PPE is used instead of engineering controls, relatively higher percutaneous absorption of phosphine by the worker may occur.

The adjustment of phosphine air concentrations to the estimated seasonal or product label maximum application rate may have led to under- or overestimation of exposure. These adjustments require the assumption that the increase or decrease in application rate causes a proportional shift in the phosphine air concentration. However, this assumption, due to variables such as wind level and direction, the air-tightness of the structure being treated, or humidity, may be incorrect, leading to under- or overestimation of exposure. The estimated seasonal application rate is greater than the bulk of the application rates used in the exposure studies. The maximum product label application rate is greater than all of the application rates used in these studies (Table 24).

Table 24. Comparison of Exposure Study, Estimated Seasonal, and Product Label Maximum Application Rates[a]

Treatment Site	StudyApplication Rates (grams/ft^3)	Estimated Seasonal Application Rate (grams/ft^3)	Product Label Maximum Application Rate (grams/ft^3)
grain elevator	0.016 - 0.048	0.06	0.145
farm bin	0.058 - 0.1	0.06	0.145
flat storage facility [b]	0.036 - 0.081	0.06	0.145
warehouse	0.02	0.06	0.145
bulk car	0.029 - 0.052	0.06	0.145
box car [c]	0.029 - 0.044	0.06	0.145
spot fumigation	0.01	0.06	0.1

[a] For seasonal exposure estimates, the measured air concentrations of the study were adjusted by multiplying the concentration with the estimated seasonal application rate, and then dividing by the application rate used in the study. The mean of these values was used to estimate exposure. For acute exposure estimates, the measured air concentrations were adjusted by multiplying the concentration with the maximum product label application rate, and then dividing by the application rate used in the study. The highest of these adjusted air concentrations was used to estimate acute exposure.

[b] The exposure data for the flat storage facility was used as surrogate exposure data for the ship hold exposure scenarios.

[c] The exposure data for the box car was used as surrogate exposure data for the ship container exposure scenarios.

Due to a lack of data, exposure estimates generated for a particular site, formulation, and fumigation type acted as surrogate estimates. The exposure estimates generated for a certain type of structure undergoing commodity fumigation were chosen to act as surrogate estimates for the same structure undergoing space fumigation or the same type of structure being fumigated with a different formulation. In addition, these exposure estimates were selected to act as surrogate estimates for similar structures undergoing commodity or space fumigation using the same formulation or a different formulation. These decisions were based upon the current product labels for aluminum phosphide, magnesium phosphide, and phosphine. The assumptions that these surrogate exposure estimates are representative may incorrect and, as a result, the surrogate exposure estimates may under- or overestimate exposure. However, due to a lack of data, these assumptions were made.

Dermal Penetration

As stated earlier, phosphine may be absorbed percutaneously, contributing to the overall exposure. However, due to a lack of data, percutaneous absorption was not factored into the exposure estimates. This may have led to underestimation of exposure.

Data Quality Control Issues

In addition to assumptions, potential data quality control issues may have led to under- or overestimation of exposure. The NIOSH method (Method No. S322) used to assay phosphine in the TWA samples uses spectrophotometry to measure the levels of phosphorous (NIOSH Report 149.10, 1986). It was assumed that the phosphorous measured in these samples was derived from only phosphine. However, since background samples were either not taken or found to be unusable in the NIOSH and registrant studies, contaminants within the air at the monitoring site may have contributed to the level of absorption measured in these samples. This may have led to overestimation of exposure.

The field-fortifications conducted for the TWA samples were assumed to be accurate and were utilized to correct for sample recovery. However, the use of these field-fortifications may have led to the underestimation of sample loss and exposure since air was not pumped through the sample column subsequent to spiking with phosphine. In addition, field-fortifications were not conducted at every study site, necessitating the use of field-fortifications from some sites to be used as surrogates for other sites.

In addition to field-fortification samples, the investigators tested for sample loss via measuring the amount of sample which broke through each column. If breakthrough was found to be excessive, then the sample was rejected. The sampling column contains two sections of an adsorbent, separated by a plug of glass wool. In order to measure breakthrough, the amount of analyte measured on the backup section of the column is compared to that measured on the front section. Analyte which has passed through the first section and adsorbed onto the backup section is considered to have broken through the column. The NIOSH investigators established column breakthrough for the analytical method (i.e., Method No. S322) used in the monitoring studies. The column(s) used in the breakthrough study were 12 centimeters long and contained 2 sections of treated silica gel (45/60 mesh) with 300 mg on the front section and 150 mg on the backup section. A total of 20.75 L of air containing phosphine at a concentration of 0.957 mg/m^3 was pumped through the column at a flow –rate of 0.2 L/min (sampling time = 104 minutes). The relative humidity (RH) and temperature during the experiment was 90% and 19 degrees C, respectively. Under these conditions, the NIOSH investigators found that the column could adsorb a total of 19.86 µg of phosphine. As a result of the study, the investigators recommended in the protocol that "to minimize the probability of overloading the sampling tube, the sample size recommended is less than two-thirds the 5% breakthrough capacity at >80% RH at twice the OSHA standard (i.e., 0.6 ppm)" (NIOSH Report 149.10, 1986). In other words, the maximum amount of phosphine adsorbed to the column should be less than 13.2 µg when the phosphine air concentration is 0.6 ppm and the RH is >80%. The authors also state that when the amount of analyte on the backup section of the column is greater than 25% of that on the first section, then the “probability of sample loss exists”.

The NIOSH Method No. S322 protocol was utilized in the NIOSH study on worker exposure in the grain-elevator and the registrant task force study on worker exposure during fumigation or aeration of commodities within the grain-elevator, farm bin, flat storage facility, warehouse, bulk cars, and box cars. The registrants also utilized the method in studies on worker phosphine exposure during spot fumigation and worker and bystander exposure during burrowing pest fumigation. However, the investigators of the registrant study altered the protocol in certain situations. For sampling periods which were greater than 30 minutes, a flow-rate of 0.2 L/min was used along with the same type of sampling column as that described in the NIOSH protocol. However, for sampling periods less than 30 minutes, an increased flow-rate of 0.5 L/min was used along with a column containing different media (i.e. 25/40 mesh). The registrants state that this increased flow-rate was validated in the laboratory and that they were given “verbal assurances from the NIOSH chemist responsible for developing the method that this increased sampling rate should not adversely affect the method”. However, it’s unclear if the validation and verbal assurance were for the increased flow-rate using the 45/60 mesh silica gel column of the NIOSH protocol or the 25/40 mesh silica gel columns actually used. In other situations, the registrant used a sampling flow rate of 0.1 L/min, presumably in the column containing the 45/60 mesh [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

The registrants used a different breakthrough standard for sample rejection than that recommended in the NIOSH Method No. S322 protocol. As stated earlier, the protocol recommends that at a flow-rate of 0.2 L, a RH >80%, and a phosphine air concentration of 0.6 ppm, the maximum amount of phosphine adsorbed to the column media should be less than 13.2 µg. Moreover, the authors go on to state that if the amount of phosphine on the backup section of the column is greater than 25% of that on the first section, then sample loss is probable. However, the investigators of the registrant study used the following sample rejection criteria: if the total amount of phosphine adsorbed to the column media is greater than 10 µg, and the amount of phosphine on the backup section of the column is greater than that found on the front section, then sample loss was likely. The registrant’s limitation of 10 µg is less than limit recommended by NIOSH (i.e. 13.2 µg). However, the level of breakthrough tolerated in the registrant study protocol is substantially higher (i.e., >100% vs. >25%), than that recommended in the NIOSH protocol for probable sample loss. The registrants state that the column capacity for phosphine increases with decreasing humidity. However, the humidities listed, for example, in the grain-elevator study sites of the registrant study range from 20 to 100%, so it’s unclear which sample columns may have had relatively higher or lower capacity for phosphine adsorption. The highest amount of phosphine recovered from a breathing-zone sampling column in the grain-elevator study was 35 µg. This is much higher than the 10 µg limit and given the high tolerance for breakthrough, sample loss at this amount and others well above 10 µg may have occurred [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015].

Grain-Elevator

In addition to the general assumptions mentioned earlier, the primary sources of uncertainty with the exposure estimates for the grain-elevator applicator and occupational bystander are the assumptions made about the number of sample replicates, and the lack of information on the location and timing of occupational bystanders working outside of or both inside and outside of the grain-elevator. According to the Background for Application Exposure Monitoring Test Guidelines (OPPTS 875.1000) of the Office of Prevention, Pesticides, and Toxic Substances at the EPA, a minimum of 9 replicates is acceptable under certain conditions: "(10) The Agency requires that each exposure situation be evaluated using at least 15 replicates. Each replicate is a measure of the exposure to one worker for one exposure period. To obtain a single ''typical'' exposure for the situation being studied, individual values must be obtained under as many different conditions that are expected to affect exposure significantly as is possible. Three variables that are expected to have the significant effect on exposure are differences in application equipment, wind conditions during outdoor application, and, most importantly, different work practices and attitudes toward safety of the study subjects. Therefore, to obtain a reasonable cross-section of the variation of individual exposure values, the Agency requires that 15 replicates be obtained from a minimum of 5 replicates from each of a minimum of three application sites. It is strongly recommended that the replicates be obtained using as many different workers as possible. Fewer replicates will be acceptable under special circumstances. For example, when applying an experimental pesticide by air where the availability of subjects is limited, a minimum of nine replicates obtained from three replicates each at a minimum of three sites was sufficient."

The combined numbers of TWA sample replicates from both the NIOSH and registrant studies ranged above and below the minimum number of recommended replicates and sites. For the applicators operating the auto-dispenser, 16 replicates were generated at 5 different sites. For the manual applicator, 4 replicates were generated at 2 different sites. The occupational bystander exposure estimates were generated for three different scenarios: fumigant application, post-application/fumigation, and post-aeration. For the fumigant application scenario, 19 replicates from 5 different sites were available for the bystander working at or above the bin-top area. Six replicates from 3 different sites were available for the bystander working below the bin-top area, and 9 replicates from 3 different sites were available for the bystander working both inside and outside of the grain-elevator. For the post-application/fumigation scenario, 14 replicates at 1 site were generated for the bystander working inside and outside of the grain-elevator. However, only 3 replicates at 2 different sites were generated for the bystander working at or above the bin-top area, and 2 replicates at 1 site for the bystander working below the bin-top location. For the post-aeration scenario, 1 replicate was generated at 1 site for the occupational bystander working both inside and outside of the grain-elevator, 6 replicates at 2 different sites for the worker located outside of the grain-elevator, 2 replicates at 1 site for the bystander located at or above the bin-top level, and 1 replicate at 1 site for the bystander located below the bin-top level. Most of the scenarios mentioned above have a relatively low number of replicates which may have led to the under- or overestimation of exposure.

Another source of uncertainty for the grain-elevator exposure data is the lack of detailed information on the location of the occupational bystanders working outside, or both inside and outside of the grain-elevator. The distance between the occupational bystanders working outside and grain-elevator is unknown. Moreover, for the occupational bystander working both inside and outside of the grain-elevator, the location(s) of the bystander while in the elevator or the amount of time spent at the location(s) are unknown. This lack of characterization creates uncertainty about the source(s) of exposure for these workers.

U.S. EPA RED Exposure Estimates for the Applicator and Occupational Bystanders Associated with Commodity Fumigation and Aeration in Concrete Upright Bins of Grain-Elevators

The numbers of applicator and occupational bystander scenarios associated with grain-elevator commodity fumigation in the RED are lower than those generated in the EAD. The RED has one applicator scenario reported as the "fumigator". Both the auto-dispenser and manual application methods were used in the registrant study. Hence, the breathing-zone air concentrations for these workers may have been combined for a single exposure estimate. Three occupational bystander scenarios were reported in the RED. These scenarios were for exposures during fumigation, post-fumigation but before aeration, and post-aeration. The bystanders were not organized according to their location relative to the bin-top level or whether they worked inside or outside of the grain-elevator. In addition, a fourth occupation bystander scenario for post-aeration "commodity transfer grain-transfer" was listed in the RED. This scenario was listed separately from the grain-elevator concrete upright bins scenarios. However, it was combined with these scenarios in Table 24. This scenario was generated from data at two of the grain-elevator sites in the registrant study and is equivalent to the "occupational bystander (outside of grain-elevator)" scenario listed under "post-aeration" in Table 14. No inhalation concentration was listed for the residential bystander scenario in the RED. The inhalation air concentrations were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. There were no statements in the RED about correction of the measured air concentrations for recovery or adjustment of the measured air concentrations to the maximum product label or estimated seasonal application rates. The inhalation concentrations listed in the Table 24 were not adjusted for PPE (i.e., respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for a given scenario was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. These inhalation air concentrations were expressed in mg/L. The air concentrations were converted from mg/L to ppm (at 25 degrees C) for ease of comparison to the EAD exposure estimates (Table 24). In addition, the inhalation concentrations were adjusted using protection factors for the use of PPE. However, these values were not reported in the RED. These values were reportedly used to generate MOE's to compare to the baseline MOE's.

Table 24. U.S. EPA Reregistration Eligibility Decision (RED) Document Phosphine Inhalation Concentrations of Grain-Elevator Workers during and after Commodity Fumigation and after Commodity Aeration in Concrete Upright Bins [a]

Exposure Scenario	Highest Measured Air Concentration (mg/L)	Highest Measured Air Concentration (ppm)	Mean Phosphine Air Concentration (mg/L)	Mean Phosphine Air Concentration (ppm)
applicator	6.3×10^{-4}	0.45	1.4×10^{-4}	0.1
occupational bystander (during fumigation)	8.5×10^{-4}	0.61	1.1×10^{-4}	0.08
occupational bystander (post-fumigation, before aeration)	3.1×10^{-4}	0.22	9.9×10^{-5}	0.07
occupational bystander (post-aeration)	1.4×10^{-4}	0.1	5.4×10^{-5}	0.04
occupational bystander (commodity transfer-grain transfer: post-aeration) [b]	7.0×10^{-5}	0.05	4.50×10^{-5}	0.03

[a] Grain-elevator worker phosphine inhalation air concentrations measured during and after fumigation and post-aeration of grain. Values were not adjusted for use of PPE. Data were obtained from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest measured air concentrations were used to calculate short-term margins of exposure (MOE's), while means of the measured air concentrations were used to calculate intermediate and chronic MOE's.

[b] The occupational bystander (commodity transfer-grain transfer: post-aeration) is equivalent to the occupational bystander (outside of grain-elevator) under post-aeration in Table 14.

Farm Bin

In addition to the previously mentioned general assumptions, the main source of uncertainty in the farm bin breathing-zone monitoring studies is the lack of data for certain scenarios. The scenario for the handler applying tablets had 16 replicates. However, only 3 replicates were generated for the occupational bystander who monitored phosphine levels during application. Moreover, no data was generated in the study for the aerator, or the occupational and residential bystanders that are potentially adjacent to the treated farm bin. To estimate exposure for the aerator, exposure estimates from a warehouse aeration study were utilized as surrogate estimates. The exposure estimates for the occupational and residential bystanders were generated using the 8-hr TWA PEL and the 24-hr TWA equivalent of the PEL, respectively. In addition, due to a lack of data, the exposure estimates for the farm bin were chosen to act as surrogate estimates for the grain storage tank which is also listed on the product labels. The use of surrogate exposure estimates may have led to under- or overestimation of the actual exposures associated with fumigation and aeration of grain within these structures.

U.S. EPA RED Exposure Estimate for the Worker Applying Fumigant to Grain in the Farm Bin

One worker exposure estimate was generated in the RED for commodity fumigation in the farm bin. The mean of the inhalation concentrations and the highest measured air concentration of the fumigant applicator are reported in the RED as being 1.2×10^{-3} mg/L or 0.9 ppm at 25 degrees C, and 4.1×10^{-3} mg/L or 3 ppm at 25 degrees C, respectively.

These values were derived from data in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. There were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label application rates. The inhalation concentrations were not adjusted for PPE (i.e. respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for the applicator or fumigator was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. The inhalation air concentrations were expressed in mg/L. The inhalation concentrations were adjusted using protection factors for the use of PPE. However, these values were not reported in the RED. These values were reportedly used to generate MOE's to compare to the baseline MOE's.

Flat Storage Facility

In addition to the previously mentioned general assumptions, the primary source of uncertainty in the exposure studies for the flat storage facility is the lack of data. The scenario of the handler applying tablets had 27 replicates. However, no data was generated in the study for the aerator, or the occupational and residential bystanders that are potentially adjacent to the treated flat storage facility. To estimate exposure for the aerator, exposure estimates from a warehouse aeration study were utilized as surrogate estimates. The exposure estimates for the occupational and residential bystander were generated using the 8-hr TWA PEL for the occupational bystander and the 24-hr TWA equivalent for the residential bystander. Due to a lack of data, the exposure estimates for the flat storage facility were chosen to act as surrogate estimates for the bunker, ground storage, and silo which are also listed on the product labels. The use of surrogate exposure estimates may have led to the under- or overestimation of the actual exposures associated with fumigation and aeration of grain within these structures.

U.S. EPA RED Exposure Estimate for the Worker Applying Fumigant to Grain in the Flat Storage Facility

One worker exposure estimate was generated in the RED for commodity fumigation in the flat storage facility. The mean of the inhalation concentrations and the highest measured air concentration of the fumigant applicator are reported in the RED as being 7.3×10^{-3} mg/L (5.3 ppm at 25 degrees C), and 2.5×10^{-2} mg/L (18 ppm at 25 degrees C), respectively [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. There were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label application rates. The inhalation concentrations were not adjusted for PPE (i.e. respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measure air concentration of the registrant study for the applicator or fumigator was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. The inhalation concentrations were adjusted using protection factors for the use of PPE. However, these values were not reported in the RED. These values were reportedly used to generate MOE's to compare to the baseline MOE's.

Warehouse

In addition to the previously mentioned general assumptions, the primary source of uncertainty in the exposure studies for the warehouse is the lack of data. The exposure estimates for the applicator, aerator, and retriever were based upon 5, 10, and 6 replicates, respectively. However, no data was available in the study for the occupational and residential bystander exposure scenarios. Hence, as with previous studies, the estimates were generated using the 8-hr TWA PEL for the occupational bystander and the 24-hr TWA equivalent for the residential bystander. Due to a lack of data, the exposure estimates for the warehouse were chosen to act as surrogate estimates for the mill and food processing plant. The use of these surrogate estimates may under- or overestimate actual exposures associated with fumigation and aeration of commodities within these structures.

U.S. EPA RED Exposure Estimates for the Applicator, Aerator, and Occupational Bystanders Associated with Commodity Fumigation and Aeration in the Warehouse

The number of exposure scenarios listed in the RED for warehouse fumigation differs from the number generated in the EAD. Both the EAD and RED have a fumigant applicator scenario and aerator scenario. However, the EAD has three occupational bystander scenarios and a residential bystander scenario, whereas the RED contains one occupational bystander scenario. Two of the occupational bystander scenarios in the EAD had no exposure data, however, so the 8-hr TWA PEL of 0.3 ppm was used as a surrogate air concentration for estimating exposure. This was also the case for the residential bystander exposure scenario. There were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label application rate or estimated seasonal application rate. The inhalation concentrations listed in the Table 25 were not adjusted for PPE (i.e. respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for a given scenario was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. These inhalation air concentrations were expressed in mg/L. The air concentrations were converted from mg/L to ppm (at 25 degrees C) for ease of comparison to the EAD exposure estimates (Table 25). In addition, the inhalation concentrations were adjusted using protection factors for the use of PPE. However, these values were not reported in the RED. These values were reportedly used to generate MOE's to compare to the baseline MOE's.

Table 25. U.S. EPA Reregistration Eligibility Decision (RED) Document Phosphine Inhalation Concentrations of Warehouse Workers during Commodity Fumigation, Aeration, and Post-Aeration [a]

Exposure Scenario	Highest Measured Air Concentration (mg/L)	Highest Measured Air Concentration (ppm)	Mean Phosphine Air Concentration (mg/L)	Mean Phosphine Air Concentration (ppm)
applicator or fumigator	7.2×10^{-4}	0.52	2.8×10^{-4}	0.2
aerator	2.1×10^{-4}	0.15	1.3×10^{-4}	0.09
occupational bystander (post-aeration)	9.7×10^{-5}	0.07	5.8×10^{-5}	0.04

[a] Inhalation concentrations are the highest measured inhalation air concentrations and the means of the inhalation air concentration samples taken from warehouse workers during fumigant application, aeration of the fumigated commodity, and post-aeration. Data were derived from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. Values were not adjusted for use of PPE. The highest measured air concentrations were used to calculate short-term margins of exposure (MOE's), while the means of the measured air concentrations were used to calculate intermediate and chronic MOE's.

Bulk Car

In addition to the previously mentioned basic assumptions, two major sources of uncertainty with the exposure estimates for the bulk car are the lack of data for certain scenarios, and the short sampling times. The exposure scenarios for bulk car fumigant application are the applicator, assistant worker, and the nearby worker. The exposure scenarios for aeration of fumigated bulk cars are the aerator, assistant aerator, and nearby worker. A scenario associated with both application and aeration is the packaging line for consumer products worker. The amount of data for the applicator fumigating the bulk car was relatively high at 12 replicates. This was also the case for the "assistant worker" (i.e., 9 replicates), who assisted the applicator but did not handle fumigant. However, only 2 replicates were generated for the "nearby worker" who is potentially exposed to phosphine post-application. Moreover, no data was generated for phosphine exposure to the nearby worker during application. In addition, exposure estimates generated for this worker are less meaningful since the exact location of this bystander relative to the fumigating car is unknown. The mean sampling durations for the aforementioned replicates are 22 minutes for the applicator, 22 minutes for the assistant worker, and 63 minutes for the nearby worker. Yet, the 8-hr TWA air concentrations used to estimate exposure for each of these scenarios was assumed to be equal to those measured over these relatively short time-spans. The assumption being that the applicator and assistant worker would be applying fumigant to bulk cars throughout the 8-hr work shift and that the nearby worker would be in the general vicinity after the application. The uncertainties and assumptions associated with these estimates may have led to under- or overestimation of exposure.

The other set of exposure scenarios for the bulk car are for aeration. These scenarios are the aerator, the assistant aerator, and the post-aeration nearby worker. As with the application portion of the study, the exact location of the nearby worker relative to the aerating car was not defined. Moreover, no data was generated for phosphine exposure to the nearby worker during aeration. The numbers of replicates generated for the scenarios were only 3, 1, and 1 for the aerator, assistant aerator, and the post-aeration nearby worker, respectively. The corresponding sample durations were 21, 36, and 157 minutes, respectively. Yet, the 8-hr TWA air concentrations used for estimating exposure were assumed to equal to the air concentrations measured over these relatively short time-spans. The assumption being that the aerator and assistant aerator would be aerating bulk cars throughout the 8-hr work shift and that the nearby worker would be in the general vicinity throughout this time after the aeration. The uncertainties and assumptions associated with these estimates may have led to under- or overestimation of exposure.

U.S. EPA RED Exposure Estimates for the Applicator, Aerator, and Occupational Bystanders Associated with Bulk Car Fumigation and Aeration

The RED contained inhalation concentrations for the fumigant applicator, bulk car aerator, and three types of occupational bystanders. The occupational bystander inhalation concentration estimates were for during fumigant application, post-application but before aeration, and post-aeration. The “assistant worker”, who aided the fumigant applicator, the “assistant aerator”, and the “nearby worker” were three of the worker scenarios described in the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. However, in the RED, these specific scenarios aren’t mentioned. Also, there were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label application or estimated seasonal application rates. The packaging line worker occupational bystander listed in Table 15 was referred to as a “bystander (post-aeration)” in the RED and listed under “commodity transfer-packaging plant”. No inhalation air concentration estimates were generated for the residential bystander in the RED. The inhalation concentrations listed in the Table 26 were not adjusted for PPE (i.e. respirator, or SCBA) and were used to generate “baseline” margins of exposure (MOE’s). The MOE’s were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for a given scenario was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE’s. These inhalation air concentrations were expressed in mg/L. The air concentrations were converted from mg/L to ppm (at 25 degrees C) for ease of comparison to the EAD exposure estimates (Table 26). In addition, the inhalation concentrations were reported to have been adjusted using protection factors for the use of PPE. However, these values were not listed in the RED. These values were reportedly used to generate MOE’s to compare to the baseline MOE’s.

Table 26. U.S. EPA Reregistration Eligibility Decision (RED) Document Phosphine Inhalation Concentrations of Workers during and after Fumigation and Aeration of Bulk Cars [a]

Exposure Scenario	Highest Measured Air Concentration (mg/L)	Highest Measured Air Concentration (ppm)	Mean Phosphine Air Concentration (mg/L)	Mean Phosphine Air Concentration (ppm)
applicator	9.40×10^{-4}	0.68	3.90×10^{-4}	0.28
occupational bystander (during fumigation)	7.10×10^{-1}	0.51	2.3×10^{-4}	0.17
occupational bystander (post-fumigation, before aeration)	9.80×10^{-5}	0.07	8.71×10^{-5}	0.06
aerator	1.60×10^{-3}	1.15	9.40×10^{-4}	0.68
occupational bystander (post-aeration)	2.10×10^{-4}	0.15	1.20×10^{-4}	0.09
occupational bystander (commodity transfer-packaging plant: post-aeration) [b]	1.20×10^{-3}	0.86	1.70×10^{-4}	0.12

[a] Phosphine inhalation air concentrations of workers during and after fumigation and aeration. Values were not adjusted for use of PPE. Data were obtained from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest measured air concentrations were used to calculate short-term margins of exposure (MOE's), while means of the measured air concentrations were used to calculate intermediate and chronic MOE's.
[b] The occupational bystander (commodity transfer-packaging plant: post-aeration) was referred to in Table 18 as the occupational bystander (packaging line worker).

Box Cars

In addition to the previously mentioned basic assumptions, two major sources of uncertainty with the exposure estimates for the box car are the lack of data for certain scenarios, and the short sampling times. The exposure scenarios for box car fumigant application are the applicator, the assistant worker, and the nearby workers during application and post-application. For aeration, scenarios exist for the indoor aerator, the outdoor aerator, the assistant aerator (outdoor aeration), and the nearby worker (indoors) post-aeration. The packaging line for consumer products worker (occupational bystander) is a scenario which exists for either fumigation or aeration. For application, the amount of data for the applicator fumigating the box car was relatively high at 17 replicates. This was also the case for the "nearby worker" (i.e., 14 replicates), potentially exposed to phosphine during fumigant application and after application but before aeration (i.e., 9 replicates). However, only 1 replicate was generated for the "assistant worker" who assisted the applicator but did not handle fumigant. The mean sampling durations for the aforementioned replicates are 14 minutes for the applicator, 11 minutes for the assistant worker, and 59 minutes for the nearby worker during application, and 93.7 minutes for the nearby worker post-application but before aeration. Yet, the 8-hr TWA air concentrations used to estimate exposure for each of these scenarios was assumed to be equal to those measured over these relatively short time-spans. The assumptions made in generating these exposure estimates may have led to under- or overestimation of exposure.

The other set of exposure scenarios for the box car are for aeration. These scenarios are the aerator with one scenario for outdoor aeration and the other for indoor aeration, the assistant aerator (outdoor aeration), and the nearby worker (indoors) post-aeration. As with the application portion of the study the exact location of the nearby worker relative to the aerating car was not defined. The number of replicates for all of these scenarios is extremely low with only 1 replicate being generated for the outdoor aerator, 2 replicates being generated for the assistant aerator, and only one replicate each for the indoor aerator and nearby worker. Moreover, the sampling durations for the outdoor aerator, assistant aerator, indoor aerator, and nearby worker are 13, 13, 4, and 45 minutes, respectively. Yet, the 8-hr TWA air concentrations used for estimating exposure were assumed to equal to the air concentrations measured over these relatively short time-spans. The assumptions made in generating these exposure estimates may have led to under- or overestimation of exposure.

U.S. EPA RED Exposure Estimates for the Applicator, Aerator and Occupational Bystanders Associated with Box Car Fumigation and Aeration

The RED contained inhalation concentrations for the fumigant applicator, box car aerator, and four types of occupational bystanders. The occupational bystander inhalation concentration estimates were for during fumigation, during and post-fumigation, post-fumigation and before aeration, and post-aeration. In the registrant study, box car aerations were conducted outdoors and indoors. Hence, in Table 16, the aerator has two scenarios, one for outdoor aeration and one for indoor aeration. However, in the RED this distinction wasn't made. As mentioned earlier, two scenarios in the box car portion of the registrant study, the source of data for the RED, were described by the registrants as the "assistant aerator" and the "nearby worker" [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. However, in the RED, these distinctions aren't made. The packaging line worker occupational bystander listed in Table 16 was referred to as a "bystander (post-aeration)" in the RED and listed under "commodity transfer-packaging plant". This occupational bystander scenario was present at the two cereal processing and packaging plants of the registrant study during both bulk car and box car fumigations and aerations. As a result, the inhalation concentration estimate for this scenario was presented in the tables for each rail car. No inhalation estimates were generated for the residential bystander in the RED. There were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label or estimated seasonal application rates. The inhalation concentrations listed in Table 27 were not adjusted for PPE (i.e. respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for a given scenario was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. These inhalation air concentrations were expressed in mg/L. The air concentrations were converted from mg/L to ppm (at 25 degrees C) for ease of comparison to the EAD exposure estimates (Tables 27). In addition, the inhalation concentrations were reported to have been adjusted using protection factors for the use of

PPE. However, these values were not reported in the RED. These values were reportedly used to generate MOE's to compare to the baseline MOE's.

Table 27. U.S. EPA Reregistration Eligibility Decision (RED) Document Phosphine Inhalation Concentrations of Workers during and after Fumigation and Aeration of Box Cars [a]

Exposure Scenario	Highest Measured Air Concentration (mg/L)	Highest Measured Air Concentration (ppm)	Mean Phosphine Air Concentration (mg/L)	Mean Phosphine Air Concentration (ppm)
applicator	1.4×10^{-3}	1.01	3.6×10^{-4}	0.26
occupational bystander (during fumigation)	4.3×10^{-4}	0.31	2.50×10^{-4}	0.18
occupational bystander (during and after fumigation)	6.3×10^{-4}	0.45	2.0×10^{-4}	0.14
occupational bystander (after fumigation and before aeration)	9.1×10^{-4}	0.65	2.3×10^{-4}	0.17
aerator	1.3×10^{-3}	0.93	6.3×10^{-4}	0.45
occupational bystander (post-aeration) [b]	6.2×10^{-4}	0.45	6.2×10^{-4}	0.45
occupational bystander (commodity transfer-packaging plant: post-aeration) [c]	1.20×10^{-3}	0.86	1.70×10^{-4}	0.12

[a] Phosphine inhalation air concentrations of workers during and after fumigation and aeration of box cars. Values were not adjusted for use of PPE. Data were obtained from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest measured air concentrations were used to calculate short-term margins of exposure (MOE's), while means of the measured air concentrations were used to calculate intermediate and chronic MOE's.
[b] one replicate
[c] The occupational bystander (commodity transfer-packaging plant: post-aeration) was referred to in Table 20 as the occupational bystander (packaging line worker).

Bulk and Box Cars

In addition to aforementioned scenarios for the bulk and box cars, are an occupational bystander scenario and residential bystander scenario for both rail car types. The occupational bystander is the "packaging line worker". As mentioned in the exposure assessment section, this worker is located within the cereal processing and packaging facility and is potentially near the fumigating or aerating rail cars. There were 7 replicates generated for this scenario with a mean sampling duration of 148 minutes. As with the nearby worker, the distance between the worker and the fumigating or aerating cars was not described in the study, nor was the level of ventilation in the work area. Hence, the exposure estimates are not as meaningful as the applicator, aerator, assistant applicator, and assistant aerator exposure estimates. No data existed for the residential bystander, therefore, as with the farm bin, flat storage facility, and warehouse, the 24-hr TWA equivalent of the 8-hr TWA PEL was used as an exposure estimate. The assumptions made in generating these exposure estimates may have led to under- or overestimation of exposure.

Due to a lack of data, the exposure estimates for the rail cars were chosen to act as surrogate estimates for vehicles, and shipping containers. The surrogate estimates may under- or overestimate actual exposures associated with fumigation and aeration of commodities within these structures.

Ship Hold and Container

In addition to the basic assumptions already mentioned, the lack of exposure data was a source of uncertainty in exposure estimates generated for the fumigating and aerating ship hold and ship container. All of the exposure estimates for the application, in-transit fumigation, and aeration steps for ship holds and ship containers were generated using exposure estimates from the bulk and box cars. If the surrogate estimates are not representative of the potential exposures associated with the fumigation of ship holds and containers, then the actual exposures may be under- or overestimated by the estimates. Due to a lack of data, the exposure estimates for the ship hold were chosen to act as surrogate estimates for the barge. The surrogate estimates may under- or overestimate actual exposures associated with fumigation and aeration of commodities on the barge.

Spot Fumigation

In addition to the aforementioned basic assumptions, the primary source of uncertainty for the spot fumigation exposure estimates is the lack of data. Monitoring data existed for only two different scenarios in the spot fumigation study. The first scenario is the applicator which had 4 replicates of data. The second scenario is the worker who aerated the structure, retrieved the spent fumigant, and then deactivated the spent fumigant in a drum of water outside of the structure. This worker scenario had 3 replicates of data. However, no data were available in the study for the occupational and residential bystander exposure estimates. Hence, as with previous studies, the estimates were generated using the 8-hr TWA PEL for the occupational bystander and the 24-hr TWA equivalent for the residential bystander. Due to a lack of data, the exposure estimates for spot fumigation were chosen to act surrogate estimates for the fumigation and aeration of beehives and small sealable containers. The surrogate estimates may under- or overestimate actual exposures associated with fumigation and aeration of these structures.

U.S. EPA RED Estimated Inhalation Concentrations for the Applicator and Aerator Exposure Scenarios

The RED contains inhalation concentrations for the fumigant applicator and aerator. The data used to generate the estimates was obtained from the registrant studies [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. In the study, the aerator also retrieved and deactivated the spent fumigant following the aeration step. However, in the RED, this worker was referred to as the "aerator". Inhalation estimates were not reported in the RED for the occupational bystander or residential bystander potentially adjacent to the structure undergoing spot fumigation. There were no statements in the RED about correction of the measured air concentrations for recovery or normalization of the measured air concentrations to the maximum product label application rates. The inhalation concentrations listed in Table 28 were not adjusted for PPE (i.e., respirator, or SCBA) and were used to generate "baseline" margins of exposure (MOE's). The MOE's were generated for short-term, intermediate term, and chronic term exposures. The highest measured air concentration of the registrant study for a given scenario was used to generate the short-term MOE, while the mean of the measured air concentrations was used to generate the intermediate and chronic MOE's. These inhalation air concentrations were expressed in mg/L. The air concentrations were converted from mg/L to ppm (at 25 degrees C) for ease of comparison to the EAD exposure estimates (Tables 28). In addition, the inhalation concentrations were reported to have been adjusted using protection factors for the use of PPE. However, these values were not reported in the RED. These values were then reportedly used to generate MOE's to compare to the baseline MOE's.

Table 28. U.S. EPA Reregistration Eligibility Decision (RED) Document: Phosphine Inhalation Concentrations of Workers during Spot Fumigation and Aeration [a]

Exposure Scenario	Highest Measured Air Concentration (mg/L)	Highest Measured Air Concentration (ppm)	Mean Phosphine Air Concentration (mg/L)	Mean Phosphine Air Concentration (ppm)
applicator	4.9×10^{-3}	3.5	4.3×10^{-3}	3.1
aerator	9.6×10^{-5}	0.07	8.7×10^{-5}	0.06

[a] Phosphine inhalation air concentrations of workers during spot fumigation and aeration of equipment within a mill. Values were not adjusted for use of PPE. Data were obtained from the registrant study [Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015]. The highest measured air concentrations were used to calculate short-term margins of exposure (MOE's), while means of the measured air concentrations were used to calculate intermediate and chronic MOE's.

Burrowing Pest Fumigation

Two variables which generate uncertainty in the estimates for the exposure scenarios of burrowing pest fumigation are the weather, and the density of pest burrows at the treatment sites. For most of the exposure scenarios, the study had relatively high amounts of TWA breathing-zone data: 38 replicates for the certified applicator and 70 replicates for the non-certified applicator. Moreover, there were 26 replicates for the exposure study for the bystander entering a treated field, and 32 replicates for the bystander in a structure near the treated field. However, the weather in place during the study may differ substantially from that at other locations and times. Also, the density of animal burrows, which positively correlates with the amount of fumigant applied to a given sized plot, is difficult to quantitate and would likely differ between locations. As a result, the exposure estimates generated from this study may under- or overestimate actual exposures.

Another source of uncertainty is the use of surrogate data. In the exposure study conducted for the occupational bystander, the investigators sampled the air in structures located 15 feet from the treated field. However, recent permit conditions issued by DPR require a buffer-zone of 100 feet. Due to lack of data, the phosphine air concentration measured at 15 feet was used as a surrogate air concentration for that at 100 feet from the treated field. This use of surrogate data may have led to overestimation of exposure.

U.S. EPA RED Estimated Inhalation Air Concentrations for the Applicator and Bystanders Associated with Burrowing Pest Control Fumigation

As mentioned in the introduction, the RED document contains a summary of a burrowing pest study conducted in a journal article (Baker, 1992). This study contained data on the levels of phosphine given off by the work clothes and gloves contaminated with aluminum phosphide dust after application of the aluminum phosphide fumigant. In addition, breathing-zone phosphine air concentration data of the workers during application of aluminum phosphide were generated. This study was summarized previously in the EAD. No MOE's were generated in the RED for the burrowing pest fumigator or bystanders potentially exposed during application or fumigation.

Granular and Cylinderized Gas Formulations

Two primary sources of uncertainty in the exposure estimates used for the cylinderized gas and granular formulations are contradictory product label statements and lack of data. Three of the product labels for these formulations have contradictory statements about the proper location of the applicator during fumigation of a structure. The product label for EcoFume® contains the statement that the gas cylinder containing phosphine must be placed outside of the structures to be fumigated. However, the label also has the statement that the handler should, "never work alone when applying the fumigant from within the storage structure…". This type of contradictory language is also seen on the product label for VAPORPH$_3$OS®. Moreover, the product label for QUICKPHLO-R® contains the statement, "If QUICKPHLO-R® Granules is to be applied from within the structure to be fumigated…", but also contains the statements, "The generator may never be placed inside the structure to be fumigated", and, "Since no entry into the fumigated structure is required to apply the fumigant…". These statements create uncertainty in estimating exposure for the applicator since the handler's location may be inside or outside of the structure during fumigation. However, for exposure assessment purposes, the applicator was assumed to be outside of the structure during fumigation. This seemed like a logical assumption since the interior levels of a fumigated structure could reach a sustained phosphine air concentration of 1000 ppm at the maximum application rate.

Another source of uncertainty in the exposure estimates for the cylinderized gas and granular formulations is the total lack of 8-hr TWA breathing-zone data. There were no studies conducted to measure the TWA breathing-zone air concentrations of the applicator, aerator, occupational bystander, or residential bystander using granular and cylinderized gas formulations. Hence, surrogate exposure estimates were used to assess exposure. Unlike the other formulations, the granular and gaseous products are assumed to be applied from outside of the sealed structure to be fumigated. Therefore, these forms would not likely be used for commodity fumigation within the grain-elevator which houses a work crew. Moreover, they aren't used for burrowing pest fumigation. However, the formulations could be used to conduct space or commodity fumigation for the other structures assessed within the document. The exposure estimates generated from the exposure studies using other product formulations were chosen to act as surrogate estimates for the cylinderized gas and granular formulations. Some or all of these surrogate estimates may under- or overestimate exposure.

REFERENCES

Baker R.O. (1992). Exposure of Persons to Phosphine Gas from Aluminum Phosphide Application to Rodent Burrows. Proc. 15th Vertebrate Pest Conf. (J.E. Borreco and R.E. March, Editors) Published at University of Calif., Davis.

Beauvais, S. (2011). Respirator Assigned Protection Factors and Information on Compliance with Legal Requirements for Respirators. HSM-11004. Sacramento, CA: Worker Health and Safety Branch, Medical Toxicology Branch, California Department of Pesticide Regulation, Cal-EPA. May 31, 2000. http://www.cdpr.ca.gov/docs/whs/memo/hsm11004.pdf

CalPIP (2011). California Pesticide Information Portal (CalPIP), Pesticide Use Report database. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://calpip.cdpr.ca.gov/main.cfm

CalPIQ (2011). Case Reports obtained using the California Pesticide Illness Query (CalPIQ) search engine from the California Pesticide Illness Surveillance Program. Database queried on 3/5/11. Department of Pesticide Regulation (Worker Health and Safety Branch), California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://apps.cdpr.ca.gov/calpiq/

CARB (2008). Report on Air Monitoring of the Application of Phosphine in Merced County in December 2008. Air Resources Board, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/emon/pubs/tac/phosphine.htm

3 CCR 6400. California Code of Regulations (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Chapter 2. Pesticides. Subchapter 4. Restricted Materials. Article 1. Restricted Materials. Section 6400. http://www.cdpr.ca.gov/docs/legbills/calcode/020401.htm#a6400

3 CCR 6158. California Code of Regulations (Title 3. Food and Agriculture) Division 6. Pesticides and Pest Control Operations. Chapter 2. Subchapter 1. Pesticide Registration. Article 1. General Provisions. Section 6158. http://www.cdpr.ca.gov/docs/legbills/calcode/020101.htm#a6158

40 CFR 152.175. (2011) Code of Federal Regulations: Title 40, Part 152, Section 175. Office of the Federal Register National Archives and Records Administration.

40 CFR 156.64(a)1. (2011) Code of Federal Regulations: Title 40, Part 156, Section 64(a)1. Office of the Federal Register National Archives and Records Administration.

Cytec Industries, Inc. (2004) Registration Package Number 51882-0022. Registration Resource Center, Division of Registration and Health Evaluation, Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St, P.O. Box 4015, Sacramento, CA 95812-4015.

DPR (1997). HS-1669: A History of the Listing of Pesticides as Restricted Materials in California. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/whs/pdf/hs1669.pdf

DPR (2001). Regulating Pesticides: The California Story, pp. 48-49. Department of Pesticide Regulation. California Environmental Protection Agency, 1001 I St, P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/pressrls/dprguide/dprguide.pdf

DPR (2012a). Toxic Air Contaminant Program. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/emon/pubs/tac/tac_prog.htm

DPR (2012b). Pesticide Use Enforcement Program Standards Compendium: Vol. 3, Restricted Materials and Permitting. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/enforce/compend/vol_3/rstrct_mat.htm

DPR (2012c). Updates to Volume 3, Restricted Materials and Permitting Compendium, Including Aluminum and Magnesium Phosphide for Burrowing Rodent Control. Enforcement CAC Letter. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/county/cacltrs/penfltrs/penf2012/2012022.htm

Fachmann I., and Gokhale, M.S. (1972). Aluminum phosphide "Phosfume" a versatile fumigant. Pesticides, October 1972.

Frank, J. (2009). Method for Calculating Short-Term Exposure Estimates. HSM-09004. February 13, 2009. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/whs/memo/hsm09004.pdf

Gillenwater H.B., Redlinger L.M., Zettler J.L., Davis R., McDonald L.L., and Zehner J.M. (1981). Phosphine Fumigation of Corn In-transit on a Bulk-Dry Cargo Ship. Journal of the Georgia Entomological Society 16: 462-475.

Hayes W.J.Jr. (1982). Pesticides Studied in Man. Williams and Wilkins Publishing Co., Baltimore, Maryland.

Han Sheng-Hui, Zhuang Ya-Hui, Liu Ji-Ang, Glindemman Dietmar (2000). Phosphorous Cycling through Phosphine in Paddy Fields. The Science of the Total Environment 258: 195-203.

HSDB (2011). Phosphine CASRN: 7803-51-2. Hazardous Substances Data Bank, TOXNET (Toxicology Data Network), United States National Library of Medicine. Queried on 12/22/11. http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~KAhNc4:1

Lyubimov A.V. and Garry V.F. (2010). Phosphine. In Krieger R., Hayes Handbook of Pesticide Toxicology, (2nd vol., 3rd ed., pp. 2259-2266). Amsterdam: Elsevier, Inc.

NIOSH Composite Report (1987). Composite Report: Industrial Hygiene Characterization of Grain Elevator Workers' Exposures to Phosphine during Bulk Grain Fumigation with Aluminum Phosphide. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health.

NIOSH (1999). NIOSH Alert. Preventing Phosphine Explosions and Poisoning During Fumigation (Publication No. 99-126). U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health. http://www.cdc.gov/niosh/99-126.html

NIOSH (2010). NIOSH Pocket Guide to Chemical Hazards (Publication No. 2010-168c). U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health. http://www.cdc.gov/niosh/npg/npgd0505.html

NIOSH Report 149.10 (1986). In-Depth Industrial Hygiene Survey Report of the Bunge Corporation, Kansas City, Kansas (Report Number 149.10). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio.

NIOSH Report 149.12 (1986). In-Depth Survey Report of Early and Daniel Co., Inc., Louisville, Kentucky (Report Number 149.12). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio.

NIOSH Report 149.18 (1987). In-Depth Survey Report of Scoular Elevator, Salina, Kansas (Report Number 149.18). Industrial Hygiene Section, Industrywide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies

National Institute for Occupational Safety and Health, Centers for Disease Control, Cincinnati, Ohio.

Ott W.R. (1990). A Physical Explanation of the Lognormality of Pollutant Concentrations. Journal of the Air and Waste Management Association 40: 1378-1383.

Phos-Fume Chemicals Co. Ltd. (1983) Registration Package Number 225-022. Registration Resource Center, Division of Registration and Health Evaluation, Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St, P.O. Box 4015, Sacramento, CA 95812-4015.

Phosphine Worker Exposure, Degesch America (2002) Registration Package 51882-015. Registration Resource Center, Division of Registration and Health Evaluation, Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St, P.O. Box 4015, Sacramento, CA 95812-4015.

PISP (2011). California's Pesticide Illness Surveillance Program: Preventing Pesticide Illness. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/whs/pisp/brochure.pdf

Powell, S. (2003). Why Worker Health and Safety Uses Arithmetic Means in Exposure Assessment. HSM-03022. September, 22, 2003. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/whs/memo/hsm03022.pdf

PUR (2011). California's Pesticide Use Report Database. Department of Pesticide Regulation, California Environmental Protection Agency, 1001 I St., P.O. Box 4015, Sacramento, CA 95812-4015. http://www.cdpr.ca.gov/docs/pur/purmain.htm

Redlinger L.M., Zettler J.L., Leesch J.G., Gillenwater H.B., Davis R., and Zehner J.M. (1979). In-transit Shipboard Fumigation of Wheat. Journal of Economic Entomology 72: 642-647.

Redlinger L.M., Leesch J.G., Davis R., Zettler J.L., Gillenwater H.B., Zehner J.M. (1982). In-transit Shipboard Fumigation of Wheat. Journal of Economic Entomology 72: 1147-1152.

Reed C. (2001). Influence of Environmental, Structural, and Behavioral Factors on the Presence of Phosphine in Worker Areas During Fumigations in Grain Elevators. Journal of Agricultural Safety and Health 7: 21-34.

Tkachuk R. (1972). Phosphorus Residues in Wheat Due to Phosphine Fumigation. Cereal Chemistry 49: 258-267.

Tomlin, CDS. (1997). The Pesticide Manual. 11th edition. British Crop Protection Council, 49 Downing Street, Farnham, Surrey GU9 7PH, UK, pp. 966-967.

Wainman H.E., Chakrabarti B., and Woodward M.A. (1980). Control of Insects in Baled Skins by Fumigation with Methyl Bromide and Phosphine. International Pest Control 22(2): 28-33.

Zettler J.L., Gillenwater H.B., Redlinger L.M., Leesch J.G., Davis R., McDonald L.L., and Zehner J.M. (1982) In-Transit Shipboard Fumigation of Corn on a Tanker Vessel. Journal of Economic Entomology 75: 804-808.

U.S. EPA (1998). Reregistration Eligibility Decision (RED) AL & Mg Phosphide. Office of Pesticide Programs, United States Environmental Protection Agency, Washington, D.C. http://www.epa.gov/oppsrrd1/reregistration/REDs/0025red.pd

APPENDICES

Appendix 1: Pesticide Use Report Database Site/Crop Terms for Aluminum Phosphide (2006-2010)

Commodity (nuts and grains)

almond	oats, general
barley (all or unspec.)	peanuts (all or unspec.)
barley (forage)	peanuts (forage-fodder)
barley (grain crop)	peanuts (human consumption)
barley, general	pecan
beans (all or unspec.)	pistachio (pistache nut)
beans, dried-type	rice (all or unspec.)
commodity fumigation	rice (grain crop)
corn (all or unspec.)	rice, wild (grain crop)
corn (forage-fodder)	rye (all or unspec.)
corn, field and/or forage (all or unspec.)	safflower (all or unspec.)
corn, field, dent (grain crop)	safflower (general)
corn, human consumption	sesame (all or unspec.)
corn, pop (pop corn grain)	sunflower (all or unspec.)
corn, seed (grain crop)	sunflower (confectionary varieties)
corn, sweet (fresh mkt. and grain crop)	sunflower, general
feed/food storage areas (unspec.)	walnut (english walnut, persion walnut)
grain crops (all or unspec.)	wheat (all or unspec.)
nut crops, nut trees (all or unspec.)	wheat (grain crop)
oats (all or unspec.)	wheat, general
oats (forage-fodder)	

Commodity (fruits, vegetables, and grasses)

alfalfa (forage-fodder) (alfalfa hay)	grapefruit
alfalfa sprouts	grasses grown for seed (all or unspec.)
alfalfa-grass mixture	kiwi fruit
apple	lemon
apricot	lettuce, leaf (all or unspec.)
artichoke (globe) (all or unspec.)	melons
asparagus (spears, ferns, etc.)	nectarine
avocado (all or unspec.)	okra (gumbo)
beans, succulent (other than lima)	olive (all or unspec.)
beets, general	onion (dry, spanish, white, yellow, red, etc.)
bermuda grass (forage-fodder)	onions (green)
blackberry	orange (all or unspec.)
blueberry	orange, king
bok choy (wong bok)	peach
broccoli	peas, general
brussels sprouts	peppers (fruiting vegetable) (bell, chili, etc.)
cabbage	persimmon
cabbage, savoy	plum (includes wild plums for human consumption)
carrots (all or unspec.)	pomegranate (miscellaneous fruit)
carrots (root crop)	potato (white, irish, red, russet)
carrots, general	prune
cherimoya	radish
cherry	squash (all or unspec.)
cherry, sour	strawberry (all or unspec.)
cherry, sweet	subtropical and tropical fruit (all or unspec.)
citrus fruits (all or unspec.)	sudangrass (forage-fodder) (sorghum sudanese)
collards	sweet potato
commodity fumigation	tangerine (mandarin, satsuma, murcott, etc.)
cotton, general	timothy (forage-fodder)
date	tomato
eggplant (oriental eggplant)	turnip (turnip greens)
fennel (all or unspec.)	turnip tops (forage-fodder)
fennel (sweet or florence; sweet anise, finocchio)	turnip, general
fig	turnips (all or unspec.)
fig (common)	vegetables (all or unspec.)
forage-fodder grasses (all or unspec.) (hay)	watercress
fruits (dried or dehydrated)	watermelons

Space Fumigation
bldg. and structures (non-ag. outdoor)
commercial storages or warehouses (all or unspec.)
structural pest control
commercial, institutional or industrial areas
animal husbandry premises
food processing, handling, plant area (all or unspec.)

Spot Fumigation
farm or ag. structures and equip. (all or unspec.)
food marketing, storage, and distribution equip.
storage areas and processing equipment (all/unspec.)

Burrowing Pest Fumigation
vertebrate pest control
animal burrow entrances
landscape maintenance
rangeland (all or unspec.)
rights of way and also rights-of-way (unspec) (firelanes, etc.)
uncultivated ag. areas (all or unspec.)
airport and landing fields (runways, etc.)
pastures (all or unspec.)
orchards (fruit/nut, etc.)
recreational areas, tennis courts, parks, etc.
uncultivated non-ag. areas (all or unspec.)

Appendix 2: Pesticide Use Report Database Site/Crop Terms for Magnesium Phosphide (2006-2010)

Commodity (nuts and grains)

beans, dried type	research commodity
sunflower, general	commodity fumigation
wheat, general	pistachio (pistache nut)
rice (all or unspec.)	soybeans (all or unspec.)
safflower, general	rice, wild (grain crop)
walnut (english, persian)	almonds
chestnut	garbanzos (inc. chickpeas)
corn (human consumption)	legumes and other non-grass crops for forage-fodder

Commodity (fruits, vegetables, and other)

prune	research commodity
vegetables (all or unspec.)	flavoring and spice crops
fruits (dried or dehyd)	cherry
grapes	peach
grapes (wine)	

Space Fumigation

structural pest control
storage areas and processing equipment
food processing/handling plant/area (all or unspec.)
feed/food storage areas (unspec.)

Spot Fumigation

storage areas and processing equipment

Burrowing Pest Control

landscape maintenance
rights of way
vertebrate pest control
uncultivated non-agric. areas
nut crops, nut trees (all or unspec.)

Appendix 3: Pesticide Use Report Database Site/Crop Terms for Phosphine (2006-2010)

Commodity (nuts and grains)

almond
commodity fumigation
pistachio (pistache nut)
rice, wild (grain crop)
walnut (english walnut, persian walnut)
beans (all or unspec)
beans, dried type
cashew
peanuts (human cons.)
pecan
sunflower

Commodity (fruits, vegetables, and other)

commodity fumigation
corn (human consumption)
fig
fruits (dried, dehyd.)
peas, general
tomato
tomatoes for proc./canning
beans (all or unspec)
beans, succulent (other than lima)
apricot
soybeans (all or uns)
grapes
n-grnhs grwn plant containers
prune
vegetables (all or unspecified)

Space Fumigation

public health pest control
storage areas and proc. equip. (all/unspec.)
structural pest control
regulatory pest control
commercial, institutional, or industrial areas

Spot Fumigation

storage areas and proc. equip. (all/unspec.)